THERMAL CHARACTERISTICS OF BORON NITRIDE FILLED EPOXY COMPOSITES

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

Master of Technology

In

Mechanical Engineering

(Specialization: Thermal Engineering)

Submitted by

Amit Kumar Yadav

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Department of Mechanical Engineering

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C E R T I F I C A T E

This is to certify that the work in this thesis entitled *THERMAL CHARACTERISTICS OF BORON NITRIDE FILLED EPOXY COMPOSITES* by **Amit Kumar Yadav** has been carried out under my supervision in partial fulfillment of the requirements for the degree of Master of Technology in *Mechanical Engineering* with *Thermal Engineering* specialization during session 2011 - 2013 in the Department of Mechanical Engineering, National Institute of Technology, Rourkela.

To the best of my knowledge, this work has not been submitted to any other University/Institute for the award of any degree or diploma.

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ABSTRACT

The present thesis deals with the estimation of thermal conductivity of epoxy composites embedded with boron nitride (BN) micro-fillers. These composites with BN content ranging from 0 to 11.3 vol.% have been prepared and the thermal conductivities of the samples are measured experimentally. A numerical simulation using finite element package ANSYS is used to explain heat transfer process within epoxy matrix filled with micro-BN and the effective thermal conductivity values obtained from this method are validated with experimental results and theoretical correlation. It is observed that for 11.3 vol% of micro-BN in epoxy matrix, the increase in thermal conductivity is about 27.82 % while for 30 vol% the increase in thermal conductivity is about 440 % which is reasonably higher compared to neat epoxy resin. The results show that the BN particles show a percolation behavior at 20 vol% at which a sudden jump in thermal conductivity is noticed.

Keywords: *Boron Nitride, Epoxy Composites, FEM, Thermal Conductivity, Percolation*

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Chapter 1

INTRODUCTION

Chapter 1

INTRODUCTION

1.1 History of Composites:

The development of composite materials and related design and manufacturing technologies is one of the most important advancement in the history of materials. Composite materials are multi-functional materials having unprecedented mechanical and physical properties that can be tailored to meet the requirements of a particular application. Many composites also exhibit great resistance to high-temperature corrosion, oxidation and wear. These unique characteristics provide mechanical engineers with design opportunities which are not possible with conventional monolithic (unreinforced) materials. Composite technology also make the use of an entire class of solid materials possible in applications for which monolithic versions are unsuited because of their great strength scatter, poor resistance to mechanical and thermal shock. Further, many manufacturing processes for composites are well adapted to the fabrication of large, complex structures, which allows consolidation of parts reducing manufacturing costs. The requirement is for enforcement towards development of new product. Composite materials were developed so that homogeneous structural materials could be found that had all the desired attributes for a given application. Brick-making process can still be seen on Egyptian tomb paintings in the Metropolitan Museum of Art. The most advanced examples are performing routinely on spacecraft in demanding environment. The most visible applications pave our roadways in the form of either steel or aggregate reinforced Portland cement or concrete. Those composites are closest to our personal hygiene from our shower stalls and bath tubs made of fiber glass. Solid surface, imitation granite and cultured marble sinks and counter tops are widely used to enhance our way of livelihood. Composites are made up of individual materials referred to as constituent materials. There are two categories of constituent materials in a composite: matrix and reinforcement.

1.2 Overview of Composites:

Now-a-days, the interest in composite materials is increasing rapidly both in terms of their research and applications. A composite material is composed of reinforcement (fibers, particles, flakes, and/or fillers) embedded in a matrix (polymers, metals, or ceramics). The matrix holds the reinforcement to form the desired shape while the reinforcement improves the overall mechanical properties of the matrix.The newly combined materials hence exhibit better strength than each individual material. Composites are combinations of two or more materials in which one of the materials is called the reinforcing phase which is in the form of fibers or particles embedded in the other material called the matrix phase.

Composites are usually classified by the type of material used for the matrix. Each type of composite is suitable for different applications. The reinforcing material can be either fibrous or non-fibrous (particulates) in nature. The composite materials have advantage over other conventional materials due to their higher specific properties such as tensile, impact and flexural strengths, stiffness and fatigue characteristics which enables for structural design applications and are more versatile. Epoxy resins are polyether resins containing more than one epoxy group capable of being converted into the thermoset form. These resins, on curing, do not create volatile products in spite of the presence of a volatile solvent. The epoxies may be named as oxides, such as ethylene oxides (epoxy ethane), or 1, 2-epoxide.

Applications for epoxy resins are extensive: adhesives, bonding, construction materials (flooring, paving, and aggregates), composites, laminates, coatings, molding, and textile finishing. They have recently found uses in the air- and spacecraft industries.

Usually epoxy or polyester resin systems are used for encapsulating a variety of electronic components because of their.

- ❖ high thermal stability
- ❖ moisture resistance
- ❖ low cost

But unfortunately, they have

- ❖ high coefficient of thermal expansion
- ❖ low thermal conductivity

Boron nitride is a synthetic material, which although discovered in the early 19th century was not developed as a commercial material until the latter half of the 20th century. Boron and nitrogen are neighbors of carbon in the periodic table - in combination boron and nitrogen have the same number of outer shell electrons - the atomic radii of boron and nitrogen are similar to that of carbon. It is not surprising therefore that boron nitride and carbon exhibit similarity in their crystal structure. In the same way as carbon exists as graphite and diamond, boron nitride can be synthesized in hexagonal and cubic forms. Hexagonal boron nitride (h-BN) is equivalent in structure to graphite (see figure.1). Like graphite, its plate like microstructure and layered lattice structure give it good lubricating properties. h-BN is resistant to sintering and is usually formed by hot pressing.

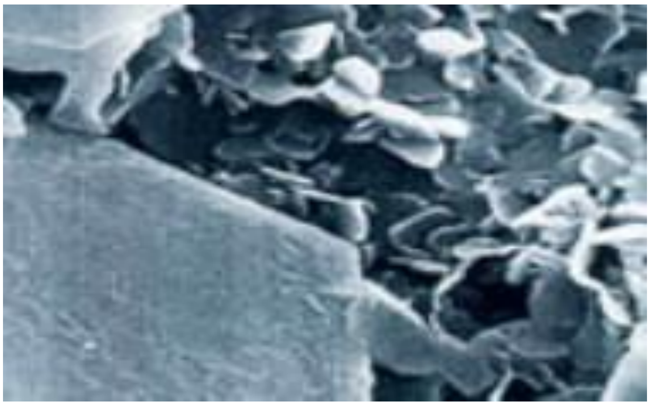

Figure1.h-BN powder (photo courtesy of Ceram Research Ltd)

Cubic boron nitride (C-BN) has the same structure as diamond and its properties resembles to those of diamond. Indeed C-BN is the second hardest material next to diamond. C-BN was first synthesized in 1957, but it is only in the last 15 years that commercial production of C-BN has been developed.

Hexagonal Boron Nitride (h-BN)

- h-BN has excellent lubricating properties.
- In the hot pressed state, h-BN is readily machinable using conventional metal cutting techniques; hence complex shaped components can be fashioned from hot pressed billet.
- Providing oxidation of the surface can be prevented, h-BN is not wetted by most molten metals.
- Glasses and salts and hence has a high resistance to chemical attack.
- High dielectric breakdown strength.
- High volume resistivity.
- Good chemical inertness.

Cubic Boron Nitride (C-BN)

- C- BN is the second hardest material known, inferior only to diamond
- High thermal conductivity
- Excellent wear resistance
- Good chemical inertness.

Wenying Zhou et.al [55] investigated the thermal conductivity of boron nitride (BN) particulates reinforced with high density polyethylene (HDPE) composites under a special dispersion state of BN particles in HDPE, i.e., BN particles surrounding HDPE particles. The thermal conductivity of composites is higher for the larger size HDPE than for the smaller sized one. The fracture behavior of boron nitride (BN) composites reinforced with several types of carbon and ceramic fibers have been examined. Fiber properties and fiber/matrix interface characteristics were found to control the mechanical strength and toughness of the composites. Because of structural similarities between BN and carbon, the mechanical behavior of C/BN was expected to be similar to that of C/C. Both composites are composed of stiff carbon fibers and matrix of relatively low modulus. Cameron G. Gofer et.al [56] incorporated highly thermal-conductive fillers of aluminum nitride (AlN) and boron nitride (BN) in the epoxy matrix in order to identify the effects of the particle size and the relative composition on the thermal conductivity of composites Jung-Pyo Honget.al [57] found that bisphenol-A methylamine-based polybenzoxazine possesses very low viscosity which aids in filler wetting and mixing. It has bimodal particle size distribution which assists in increasing the particle packing density. This filler-matrix system provides a highly thermally conductive composite due to the capability of forming conductive networks with low thermal resistance along the conductive paths. Hatsuo Ishid et.al [58] used high thermally conductive ceramic materials in polymers in order to improve the thermal conductivity of encapsulates or substrate. Jens Eichler et.al [59] studied the physical properties of BN which are mostly governed by its atomic structure. BN is isoelectronic with carbon, and therefore h-BN is also known as “white graphite” The hexagonal BN layers are bonded by weak van der Waals forces, which enable the layers to slide easily against each other.

1.3 Definition of composite:

A composite (or composite material) is defined as a material that consists of at least two constituents (distinct phases or combinations of phases) which are bonded together along the interface in the composite, each of which originates from a separate ingredient material which pre-exists the composite.

- Composite refers to a material, as opposed to a structure or a component, as such a composite material is used for the fabrication of components of various shapes or functions, thus it should be distinguished from a wing or other structure made of several components bonded together and from an electronic device or packaging structure made of layered materials (although one of the materials in the packaging could be considered a composite).
- Composites are combinations of two materials in which one of the materials called the reinforcing phase is in the form of fiber sheets or particles and is embedded in the other material called the matrix phase. The primary function of the matrix is to

transfer stresses between the reinforcing fibers or particles and to protect them from mechanical and/or environmental damage whereas the presence of fibers or particles in a composite improves its mechanical properties i.e. stiffness and strength etc.

A composite material is therefore a synergistic combination of two or more micro-constituents that differ in physical form and chemical composition, which are insoluble in each other. The objectives are to take advantages of the superior properties of both materials without compromising on the weakness of either. Composite materials have successfully substituted the traditional materials in several lightweight and high strength applications. The reasons why composites are selected for such applications are mainly their high strength-to-weight ratio, toughness, high creep resistance and high tensile strength at elevated temperatures.

1.4 Types of Composite Materials:

Broadly, composite materials can be classified into three groups on the basis of matrix material use.

1.4.1 Metal Matrix Composites (MMC).

1.4.2 Ceramic Matrix Composites (CMC).

1.4.3 Polymer Matrix Composites (PMC).

1.4.1 Metal Matrix Composites (MMC):

These composites consist of metal alloys reinforced with continuous fibers, whiskers (a version of short fibers that are in the form of single crystals), or particulates (fine particles, as distinct from fibers). They use metals as matrix materials and they have a higher temperature resistance than PMCs but in general are heavier. The basic attributes of metals reinforced with hard ceramic particles or fibers are improved strength and stiffness, improved creep and fatigue resistance, and increased hardness, wear and abrasion resistance, combined with the possibility of higher operating temperatures than for the unreinforced metal (or competing reinforced plastics).

1.4.2 Ceramic Matrix Composites (CMC):

Ceramic matrix composites (CMCs) have a ceramic matrix such as alumina calcium alumina silicate reinforced by fibers such as carbon/silicon carbide. Advantages of CMCs include high strength, low density, hardness, high service temperature limits for ceramics and chemical inertness. However, ceramics by themselves have low fracture toughness. For producing ceramic matrix composites one of the main objectives is to increase the toughness of final material. Naturally it is hoped and indeed often found that there is associative improvement in strength and stiffness of ceramic matrix composites.In many respects, ceramic materials can be considered a design engineer's dream. Typical characteristics include high strength and stiffness, both at room and elevated temperatures in caustic atmospheres; light weight and abundant raw materials, high hardness, friction resistance, and high electrical resistivity.

Classification of the composite materials with metal matrix:

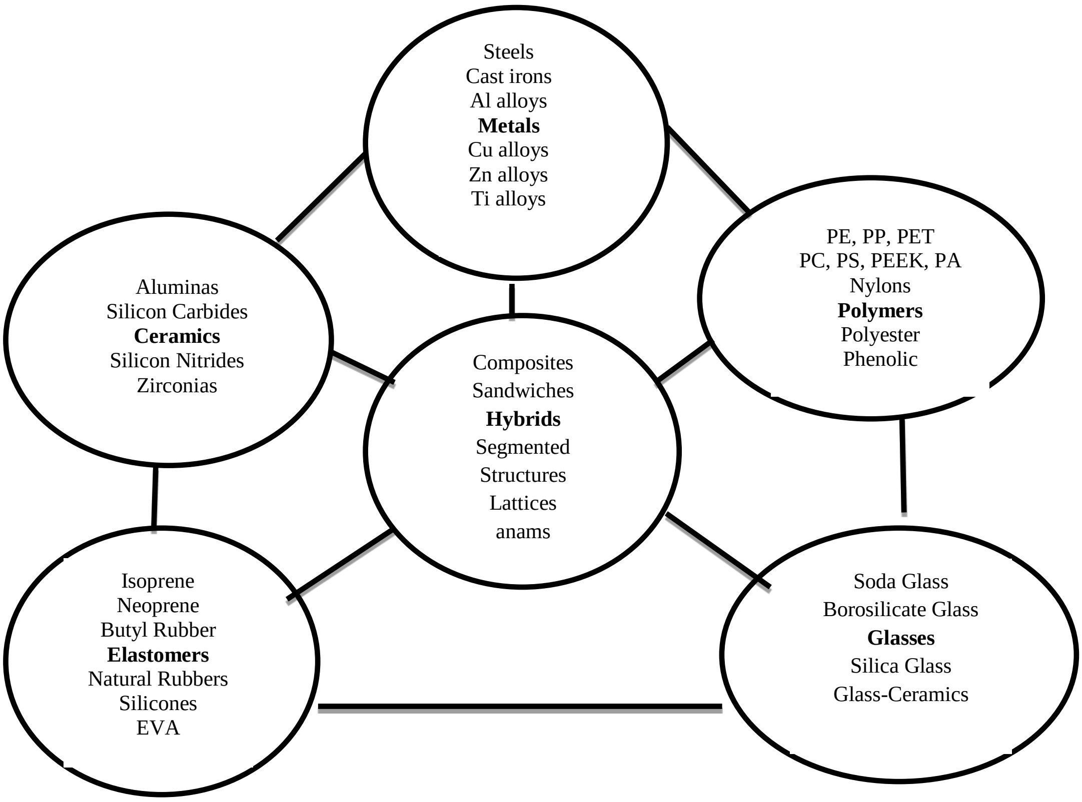

Fig 1.2: Conventional classification of composite materials in accordance to matrix material

1.4.3 Polymer Matrix Composites (PMC)

Polymeric matrix composites are inexpensive, corrosion resistant and easy to form into complex shapes, and they have low densities.They are increasingly used in automotive, aerospace and many other commercial applications. In general the mechanical properties of polymers are inadequate for many structural purposes; particularly their strength and stiffness are low compared to metals and ceramics. Secondly, high pressure and high temperature are not required in the processing of polymer matrix composites. Also simpler equipments are required for manufacturing polymer matrix composites. For this reason polymer composites developed rapidly and became popular for structural applications.

1.5 Types of Polymer Composites:

Broadly, polymer composites can be classified into three categories on the basis of reinforcing material. They are given as;

1.5.1 Fiber reinforced polymer (FRP).

1.5.2 Particle reinforced polymer (PRP).

1.5.3 Structural/ Hybrid polymer composites (SPC).

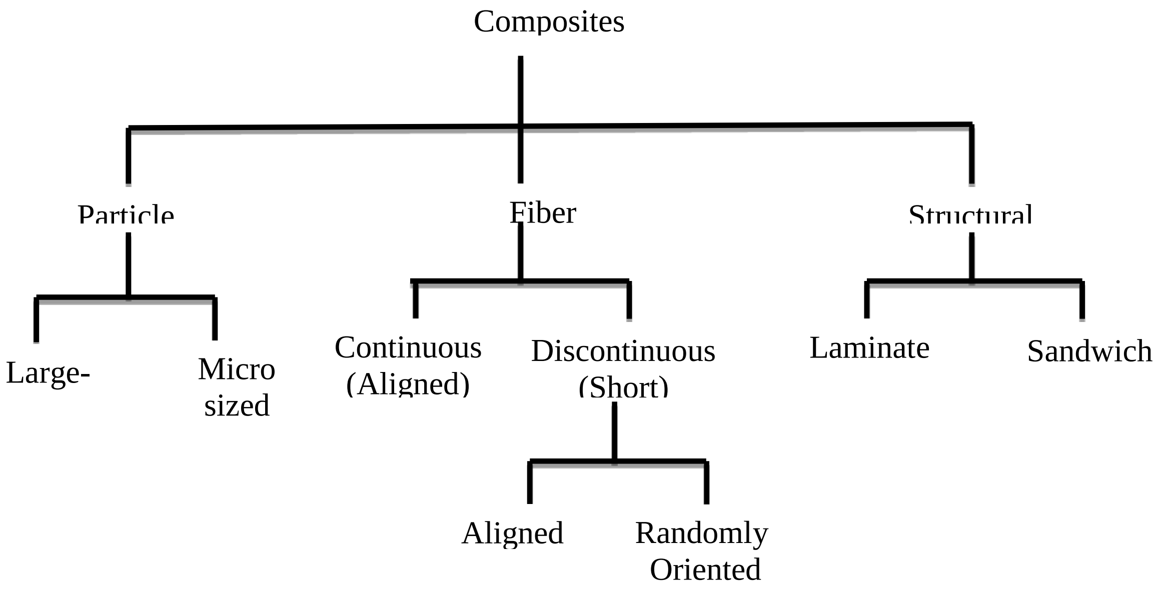

Figure 1.3 Classifications of composites based on reinforcement type

1.5.1 Fiber Reinforced Polymer (FRP)

- Containing discontinuous fibers
- Containing continuous fibers

Fiber reinforced composites contain reinforcements having length much greater than their cross-sectional dimensions. Such a composite is considered to be a discontinuous fiber or short fiber composite if its properties vary with fiber length. Fibers and matrix are the main constituents of common phase of fiber reinforced composites. Fibers are the main source of strength in composite. Main function of fibers is reinforcement and while matrix glues all the fibers together in shape and transfers stresses (load) between the reinforcing fibers. Sometimes, for desired smoothening of the manufacturing process, filler might be added to it to impart special properties to the composites and reduce the product cost. Similarly epoxy, phenolic resin, vinyl ester, polyester and polyurethanes are the common matrix materials. Among all resin material epoxy and Polyester is most widely used. Epoxy resin, which has higher adhesion and less shrinkage than polyesters resin, comes in second for its higher cost.

1.5.2 Particle Reinforced Polymer

These are the cheapest and most widely used. They fall in two categories depending on the size of the particles.

- Large-particle composites, which act by restraining the movement of the matrix, if well bonded.
- Dispersion-strengthened composites, containing 10-100 μm particles. The matrix bears the major portion of the applied load and the small particles hinder dislocation motion, limiting plastic deformation

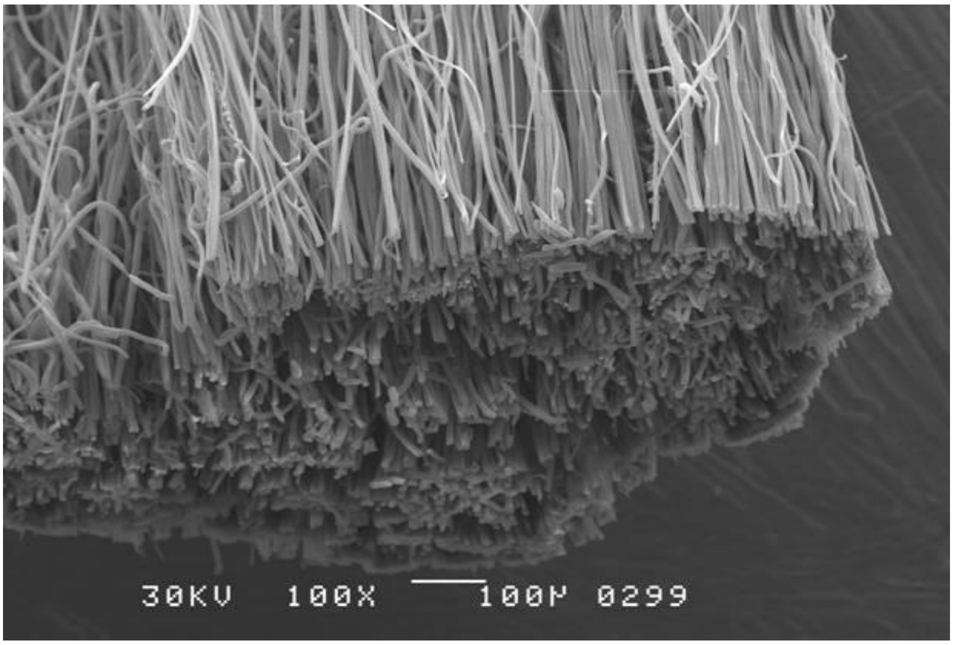

Fig 1.4: Cross-sectional view of high strength fiber tow.

In particle reinforced polymer composites, particles are used basically for increasing the ductility and decreasing the modulus of the matrix. Particles are also used for reducing the cost of the composites. Matrices and Reinforcements can be common inexpensive materials and are easily processed. High melting temperature, low density, high strength, stiffness, wear resistance and corrosion resistance are some of the useful properties of ceramics and glasses. Many ceramics are good thermal and electrical insulators. Some ceramics materials have special properties likes, magnetic, piezoelectric and superconductivity at very low temperatures. These properties are well utilized in the composite material. However, glasses and ceramics have one major disadvantage that they are brittle. An example of particle reinforced composites is an automobile tires, which has carbon black particles in a matrix of poly-isobutylene elastomeric polymer.

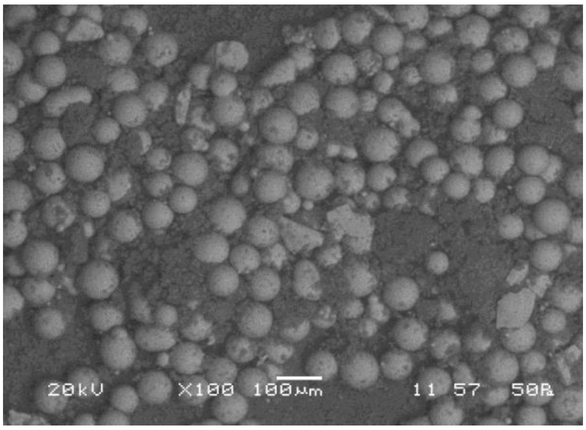

Fig 1.5: SEM micrograph of epoxy filled with boron nitride (BN) and solid glass microsphere (SGM).

1.5.3 Structural Polymer Composites

The laminar composites are composed of layers of materials held together by matrix. Sandwich structures also falls under this category. Previously, it has been found that polymers have replaced many of the conventional metals or materials in various applications. This has been possible due to the advantages of the polymers over conventional materials, ease of processing productivity and cost reduction are the most important advantages of using polymers in composite.

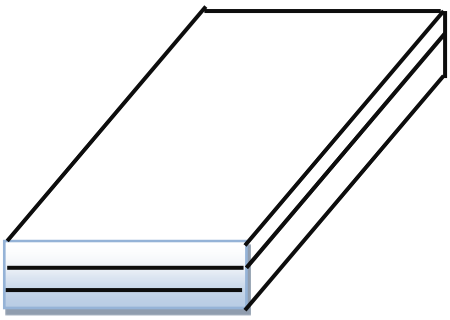

Fig 1.6 Laminate composite

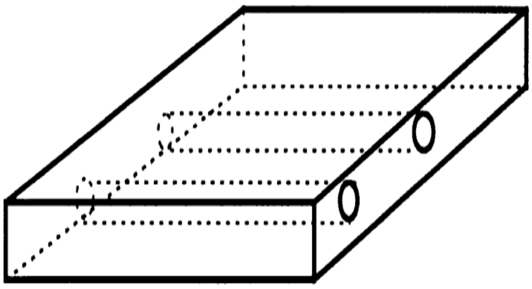

Fig. 1.7 Fiber composite

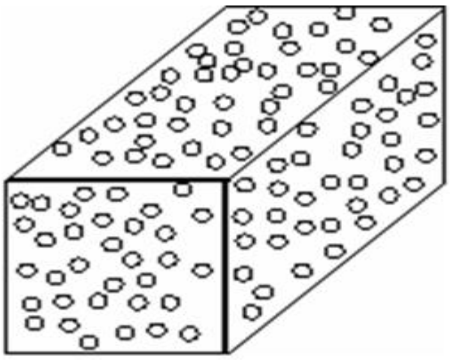

Fig 1.8 Particulate composite

They have generated wide interest in various engineering fields particularly in aerospace applications. New researches are underway worldwide to develop newer composites with varied combinations of fillers and fibers so that they can be usable under all operational conditions. The properties of polymers are modified using fillers and fibers to suit the high strength or high modulus requirements. Fiber reinforced polymers offer advantages over other conventional materials when specific properties are compared. That is the reason for these composites finding applications in diverse fields from appliances to spacecrafts.

1.6 Laminate Definition: A lamina (also called a ply or layer) is a single flat layer of unidirectional fibers or woven fibers arranged in a matrix form. A laminate is a stack of plies of composite material. Each layer can be laid at various orientations and can be made up of different material systems. The average properties of a composite ply are depending on the individual properties of the constituents. The properties are including stiffness, strength, moisture expansion and thermal coefficient. Note that average properties are derived by considering the ply to be homogeneous. At this level, one can optimize for the stiffness and strength requirements of a lamina. This is called the micromechanics of a lamina. Laminate composites are composed of layers of materials held together by matrix. Generally, these layers are arranged alternatively for the better bonding between reinforcement and the matrix. These laminates can have unidirectional/bidirectional orientation of the fiber reinforcement according to the end use of the composite. The different types of composite laminates are unidirectional, cross-ply and symmetric laminates. High strength and stiffness usually require a high proportion of fibers in the composite. This is obtained by aligning a set of long fibers in a thin sheet (a lamina /ply). However, these material are highly anisotropic generally being weak and compliant (having a low stiffness) in the transverse direction. Commonly, stiffness and high strength are required in various directions within a plane form. The solutions are stack and weld together in a number of sheets each having the fibers oriented in different direction and a stack is termed a laminate. An example is shown in the diagram (Fig.1.6). We have already discussed the concept of a laminated and a pictorial illustration of the way that the stiffness becomes more isotropic as a single ply is made into a cross-ply laminate in introduction section.

1.7 Comparison between composite and conventional material

Some general differences between composite and metal

- Comparing efficiently designed structural elements, the fatigue endurance limit for aramid and carbon fiber reinforced epoxies may approach 60% of the ultimate tensile strength of steel and aluminum.

- ❖ Unidirectional carbon fiber reinforced epoxies have specific modulus that is approximately 3 ½ to 5 times greater than that aluminum / steel. Aramid falls between carbon and glass fiber reinforced epoxies.
- ❖ High corrosion resistance of fibre composites contributes to reduced life- cycle cost.
- ❖ Fibre composites are more versatile than metals and can be tailored to meet performance needs and complex design requirements such as aero-elastic loading on the wings and the vertical & the horizontal stabilisers of aircraft.
- ❖ Long term service experience of composite material environment and durability behaviour is limited in comparison with metals.
- ❖ Impact energy values for aramid-epoxy composite are significantly higher than those for aerospace aluminum alloy and carbon fiber.
- ❖ Because fiber reinforced plastic can be designed with excellent structural damping features they are less noisy and provide lower vibration transmission than metals.

1.8 Advantage of Composites:

The high performance and unique production of the numerous structural fibers composite material and forms now available to designers are proof of their many advantages.

- ❖ Improved torsional stiffness.
- ❖ Improved weather ability.
- ❖ High dimensional stability.
- ❖ Improvement in the wear and friction properties.
- ❖ Improved or reduced thermal conductivity.
- ❖ Reduced material wastes.
- ❖ High corrosion resistance.
- ❖ Excellent impact and damage tolerance properties.
- ❖ Stiffness and strength of composite is higher than conventional metals.

1.9 Application of composite in various fields:

Applications of the composite material are based on requirement criteria like when we need that high temperature application; we use metal matrix and ceramic matrix composites. There are huge areas of application of polymer composite in various fields. In polymer composites polymers used are epoxy, phenolic, acrylic, urethane and polyamide. Each of group has specific characteristics and advantage over other polymer, therefore application is based on requirement.In road transportation polyester resin used with suitable fillers and reinforcements. The selection was dictated by properties like low cost ease in designing and production of functional parts etc. By using a variety of reinforcements polyester has continued to be used in improving the system and other applications. Thermoplastics are combined with reinforcing fibers in various proportions as the requirements. Thermo plastics are used to produce several parts of vehicle. Selection of the material is made from the volume required apart from cost-effectiveness and mechanical strength. The components are that need conventional paint finishing is generally made with thermosetting resins while thermoplastics are used to build parts that are moulded. Press moulded reinforced polyester possess the capability to produce large parts inconsiderable volume with cost-effectiveness. An application of polymer matrix composites is very large from tennis racquets to the space shuttle. Rather than enumerating only the areas in which polymer based composites are used, a few examples have been taken from each industry. Emphasis has been placed on why a composite material is the material of choice.

Aircraft:

The military aircraft industry has mainly led the use of polymer matrix composites. In the field of commercial airlines, the use of composites has been conservative because of safety concerns. Use of composites is limited to secondary structures such as rudders and elevators made of graphite/epoxy for the Boeing 767 and landing gear doors made of Kevlar–graphite/epoxy.In panels and floorings of airplanes composites are used. Helicopters and tilt rotors use graphite/epoxy and glass/ epoxy rotor blades that not only increase the life of blades by more than 100% over metals but also increase the top speeds.

Space:

Main factors make composites the material of choice in space applications is that: strength, high specific modulus and dimensional stability is one of most important mechanical properties that need to satisfy the required condition, during large changes in temperature in space. For the space shuttles, graphite/ epoxy were chosen primarily for weight savings and for small mechanical and thermal deflections concerning the remote manipulator arm which deploys and retrieves payloads.

Sporting goods:

The optimum design of sports equipment requires the application of a number of disciplines not only for enhanced performance but also to make the equipment as user-friendly as possible from the standpoint of injury avoidance. In designing of sports equipment the various characteristics of materials must be considered. Among these characteristics are ductility, density, strength, fatigue resistance, toughness, modulus (damping) and most important are cost. To meet the requirements of sports equipment the materials of choice often consist of a mixture of material types -metals, ceramics, polymers and composite concepts.

Medical devices:

Applications here include the use of glass–Kevlar/epoxy lightweight face masks for epileptic patients. Artificial portable lungs are made of graphite–glass/epoxy so that a patient can be mobile.

Chemical Industry:

Supplemented by the advantages of composites of lightweight, mould ability, fire resistance properties resistance to chemicals has made the material popular in the chemical industries. Composites material are used in storage tanks, scrubbers, ducting, exhaust stacks, pumps, piping, blowers, columns and reactors etc.

Marine:

The application of fiberglass in boats is well known. Hybrids of Kevlar–glass/epoxy are now replacing fiberglass for improved weight savings, vibration damping, and impact resistance. Kevlar–epoxy by itself would have poor compression properties.

Commercial:

The Fiber-reinforced polymers have many other commercial applications. Some brooms used in pharmaceutical factories have handles that have no joints or seams, the surfaces are smooth and sealed.

*****

Chapter 2

LITERATURE REVIEW

Chapter 2

LITERATURE SURVEY

The purpose of this literature review is to provide background information on the issues to be considered in this thesis and to emphasize the relevance of the present study. This treatise embraces some related aspects of polymer composites with special reference to their thermal characteristics. The topics include brief review.

(1) On Particulate Reinforced polymer composites.
(2) On Thermal Conductivity of Polymer composites.
(3) On Thermal behavior of BN Filled with epoxy resin.
(4) On Thermal Conductivity Models.

2.1 On particulate filled polymer composites:

Polymers are classified broadly into two groups: thermosetting and thermoplastics. Hard particulate fillers consisting of metal or ceramic particles and fiber fillers made of glass are extensively being used these days to dramatically improve the mechanical properties of PTFE such as wear resistance, up to three orders of magnitude [1]. Metal particles are used as reinforced the various kinds of polymers and polymer matrix composites which have a wide range of industrial applications such as electrodes, heaters. Polymer thermal stability is very important and composites with thermal durability at high temperature is investigated in [3] etc. These engineering polymer composites are desired due to their low density, high chemical resistance, high corrosion resistance, ease of fabrication and low cost [4-6]. Over two decades, ceramic filled polymer composites have been the subject of extensive research. R. N. Rothonhas study [7, 8] that the Mineral fillers in thermoplastics: filler manufacture and characterization .The inclusion of inorganic fillers into polymers for commercial applications is primarily aimed at the cost reduction and stiffness improvement.

Along withfiber reinforced composites, the particulate filled composites have been found to perform well in many real operational conditions like in thermal and mechanical field. Silica particles play an important role in improving electrical, mechanical and thermal properties of the polymer composites when they are added into a polymer matrix to form a composite, [9, 10]. Currently, particle size is being reduced rapidly and many studies have focused on how single-particle size affects mechanical properties [11-17]. Mechanical properties of the composites have greatly been affected by the shape, size, volume fraction, and specific surface area of such added particles. In this regard, Yamamoto et al. [18] discussed that the structure and shape of silica particle have significant effects on the mechanical properties such as fatigue resistance, tensile and fracture properties. Nakamura et al. [19-21] studies the effects of size and shape of silica particle on the strength and fracture toughness based on particle-matrix adhesion and also found an increase of the flexural and tensile strength as specific surface area of particles increased.

2.2 On Thermal Conductivity of Polymer composites:

On the other hand, unsaturated polyester (UP) resins are the most widely used thermosetting polymeric composites [22] due to advantages such as high strength, dimensional stability, low weight, good corrosion properties and low price [23].Wong et al. [24] have presented the effective thermal conductivity, elastic modulus, and coefficient of thermal expansion of epoxy resins filled with ceramic fillers like silica, alumina and aluminum nitride were determined. It was found that Agari's model provided a good estimate of the composite thermal conductivity. Important work has been reported on the subject of heat conductivity in polymers by Hansen and Ho [25], Penget.et.al [26], Tavman[27], Choy and Young [28] etc. by the increment of thermal transport significantly in the direction of orientation and decrement slightly in the direction perpendicular to the orientation. But most of these studies mainly focus on the thermal behaviorof neat polymers only and not of their composites. Various reports are available in the existing literature on experimental as well as numerical and analytical studies on thermal conductivity of some filled polymer composites [29-41].

The fillers most commonly used are Copper particles, aluminum particles, brass particles, short carbon fiber, carbon particles, graphite, magnetite particles and Copper nitrides. Exhaustive overview on models and methods for predicting the thermal conductivity of composite systems was first presented by Progelhofet. al [42].Nielsen model was used by Procter and Solc [43] as a prediction to investigate the thermal conductivity of several types of polymer composites filled with different fillers and confirmed its applicability. Nagai and Lai [44] found a modified form of Bruggeman model for Al_2O_3/epoxy system and AlN/epoxy system and found that both are good predictive theories for thermal conductivity. Griesinger et.al [45] discussed that the thermal conductivity of low-density poly-ethylene (LDPE) increased from 0.35 W/mK for anisotropic sample, to the value of 50 W/mK for a sample with an orientation ratio of 50.The mechanical and thermal properties of poly-ethylene composites filled with copper powder are found by Tavman [46] while the thermal properties such as thermal conductivity, thermal diffusivity and specific heat of metal(copper, zinc, iron, and bronze) powder filled HDPE composites in the range of fillercontent 0–24% by volume were investigated experimentally by Sofian et al. [47]. A moderate increase in thermal conductivity upto 16% of metal powder filler content was observed. As polymer compositeshavelow thermal and electrical conductivity, improvement inthese properties of polymers filled with metal powders was reported by Mamunyaet. al [49].

In a recent research Weidenfeller et al. [50] investigated about the effect of the interconnectivity of the filler particles and its important role in the thermal conductivity, thermal diffusivity and specific heat capacity of the composites. They prepared Poly propane (pp) samples with different commercially available fillers by extrusion and injection molding using various volume fractions of filler content to systematically vary density and thermal transport properties of these polymer composites. Surprisingly, they measured that the thermal conductivity of the prepared Poly propane (PP) has increased from0.27 w/mk up to 2.5W/mK with 30 vol. % talc in the (PP) matrix, while the same matrix material containing the same volume fraction of copper particles had a thermal conductivity of 1.25W/m-K despite the fact that thermal conductivity of copper particles have a value approximately 40 times greater than that of talc particles. Tekceet. al [51] studies on the shape factor of fillers has a strong influence on thermal conductivity of the composite. While Kumlutas and Tavman [52] carried out a numerical and experimental study on thermal conductivity of particle filled polymer composites, they found out that for tin particle filledHDPE, thermal conductivity increases from 0.554W/mK for pure HDPEsamples to 0.681W/mK and 1.116W/mK for 8% and 16% filler content byvolume respectively, which represents 23% and 101% increase and also. The thermal conductivity of the composites were found by various methods and comparison was done with experimental result fora high-density polyethylene (HDPE) matrix filled with tiny particles up to 16% by volume and the existence of a possible correlation between thermal conductivity and wear resistance of particulate filled composites were reported by Patnaik et. al[53]. Sanada et al.[54] studied on microstructure and thermal conductivity of polymer composites with Nano and micro fillers, in which that A Monte-Carlo algorithm in the MacroPac program from Intelligences was used to generate a unit cell with randomly distributed micro fillers.

2.3 On Thermal and dielectric behavior of BN Filled with epoxy resin.

The thermal conductivity of boron nitride (BN) particulates reinforced high density polyethylene (HDPE) composites was investigated under a special dispersion state of BN particles in HDPE, i.e., BN particles surrounding HDPE particles. The thermal conductivity of composites is higher for the larger size HDPE than for the smaller size one. The thermal conductivity increases with increasing filler content. It is found also that the combined use of BN particles and alumina short fiber obtains higher thermal conductivity of composites compared to the BN particles used alone[55].The fracture behavior of boron nitride (BN) composites reinforced with several types of carbon and ceramic fibers has been examined. Fiber properties and fiber/matrix interface characteristics were found to control the mechanical strength and toughness of the composites [56].

Because of structural similarities between BN and carbon, the mechanical behavior of C/BN was expected to be similar to that of C/C. Both composites are composed of stiff carbon fibers and matrix of relatively low modulus. High thermal-conductivity fillers of aluminum nitride (AlN) and boron nitride (BN) were incorporated in the epoxy matrix in order to identify the effects of the particle size and the relative composition on the thermal conductivity of composites. As microelectronic devices become increasingly integrated and used at high powers and high frequencies, a large amount of heat is generated and thus it should be dissipated quickly through the printed circuit boards and/or electronic devices, e.g. in such applications as light emitting diodes (LEDs), highly-integrated memory chips, etc. [57]. The generated heat could increase the temperature over the thermal-stability limit of the device to cause fatal damages.

The bisphenol-A methylamine-based polybenzoxazin possesses very low A-stage viscosity which aids in filler wetting and mixing. It has bimodal particle size distribution which assists in increasing the particle packing density. This filler-matrix system provides a highly thermally conductive composite due to the capability of forming conductive networks with low thermal resistance along the conductive paths[58]. The heat dissipation problem in microelectronic packaging is becoming increasingly important as the demands in denser and faster circuits intensify. The incorporation of highly thermally conductive ceramic materials in polymers in order to improve the thermal conductivity of encapsulates or substrate has long been studied. The physical properties of BN are mostly governed by its atomic structure. BN is isoelectronic with carbon, and therefore h-BN is also known as “white graphite” [59]. The hexagonal BN layers are bonded by weak van der Waals forces, which enable the layers to slide easily against each other. Therefore, h-BN is used as a solid lubricant or release agent either as a sintered body (e.g. side dams) or applied as suspensions or powders (e.g. aluminum extrusion or titanium shaping).

Cubic boron nitride (c-BN), if properly developed, can be a very promising material for electronic applications, such as ultraviolet (UV) detectors and UV light emitting diodes operable at wavelengths in the deep UV regime. A thermally conductive linear low-density polyethylene (LLDPE) composite with aluminum nitride (AlN) as filler was prepared in a heat press molding [61-65].Thermal interface materials and phase change materials Boron nitride (BN) forms both hard diamond-like cubic phase and softer graphite-like sp2-bonded phases analogous to carbon. Cubic BN (c-BN) films can be prepared by a variety of vapor phase deposition techniques with sufficient ion bombardment during film growth.

However, a severe drawback to SiO2f/SiO2 composites is the significantly reduced tensile strength caused by the growth of the crystals when the composites are exposed to high temperatures. The Lewis–Nielsen model describes a vast amount of available experimental data on the thermal and electrical conductivities of particulate composites quite well [66].

The improvement of heat conduction in electrical power equipment has become a very important issue. Thermoplastic and thermosetting polymers, which are mainly used for their insulating properties, have a relatively low thermal conductivity [67]. One approach to change this is to introduce inorganic fillers which have high thermal conductivities compared to the polymer matrix.

A drastic degradation of conductivity occurred when BN content increased to a high level and in some cases, the conductivity of machinable AlN/ BN ceramics was unbearably low. Nowadays, it has been a challengeable subject to keep the inherent high thermal conductivity of a ceramics from sudden decrease and to improve its machinability as well. The thermal conductivity of the neat epoxy and epoxy composites was measured by laser flash method [68-72]. The BN Nano platelets showed the weak interface for the epoxy/BN composite because neither chemical bonding nor molecular entanglement occurred between Nano platelets and matrix.

Boron nitride has a reasonably high electrical resistivity(10^{15} Ωcm) and breakdown strength (53 kV/mm) and a small relative permittivity, about 4.0, which is close to that of many polymer matrices and much smaller than that in other ceramics. It also has good heat transfer characteristics. These useful properties suggest that boron nitride may be a good inorganic filler material in the power, microelectronic and power electronic industriesChao Zhang. et.al [75].Epoxy composites are widely used in both the power industry and the microelectronics industry because of their superior electrical, mechanical and thermal properties along with their economic cost and convenient process ability. Generally, the properties of an epoxy composite depend upon the nature of the filler such as size, shape, dispersion in the matrix etc. Therefore, we choose the filler to meet the practical requirements we seek.

Epoxy resin is a widely used material, especially in high voltage insulation, as a consequence of its good mechanical and dielectric properties. Due to its preparation method using liquid phases mixing followed by curing, the dispersion of fillers is easier than for thermoplastic polymers H. Coudercet. al [79]. Boron Nitride (BN) is attractive filler because of its good insulating properties and high thermal conductivity. BN has been recognized as an electrically insulating and thermally conductive material and is also available in hexagonal (similar to graphite) or cubic (similar to diamond) forms. High temperature use composite dielectrics have been recently awaited due to recent needs for compact design of power apparatus and for high density and high voltage design for power electronics Toshikatsutanakaet.al [78]. There is a general tendency that breakdown strength decreases with the increase of filler content for cubic and hexagonal BN.

2.4 On Thermal Conductivity Models

Previously, several theoretical and empirical models have been proposed to predict the effective thermal conductivity of two-phase mixtures composite. Comprehensive review articles have discussed the applicability of many of these models [27, 86]. For a two-component composite, the simplest alternatives would be with the materials arranged in either parallel or series with respect to heat flow, which gives the upper or lower bounds of effective thermal conductivity.

For the parallel conduction model

$$k_c = (1-ø)k_m + \phi k_f \tag{2.1}$$

Where, k_c, k_m, k_f are the thermal conductivities of the composite, the matrix and the filler respectively and Ø is the volume fraction of filler.

For the series conduction model:

$$\frac{1}{k_c} = \frac{(1-ø)}{k_m} + \frac{ø}{k_f} \tag{2.2}$$

The correlations presented by equations (2.1) and (2.2) are derived on the basis of the Rules of Mixture (ROM). An equation relating the two-phase solid mixture thermal conductivity to the conductivity of the individual components and to two parameters was derived by Tsao [87] which describe the spatial distribution of the two phases. Cheng and Vachon [88] assuming a parabolic distribution of the discontinuous phase in the continuous phase, obtained a solution to Tsao's [87] model that did not require knowledge of additional parameters. A new model for x filled polymers was proposed by Agari and Uno [89], which takes into account parallel and series conduction mechanisms. According to this model, the expression that governs the thermal conductivity of the composite is:

$$\log(k_c) = ØC_2\log(k_f)+(1-ø)\log(C_1 k_m) \tag{2.3}$$

Where, C_1, C_2 are experimentally determined constants of order unity. C_1 shows a measure of the effect of the particles on the secondary structure of the polymer, like crystal size and the crystalline of the polymer. And C_2 measured easily by the particles to form conductive chains are shown by C_2. The more easily particles are gathered to form conductive chains, the more thermal conductivity of the particle contributes to change in thermal conductivity of the composites and C2 becomes closer to 1. Later, the shape of the particles was taken into account and they modified the model [90]. Generally this semi-empirical model seems to fit the experimental data well. However, for determination of the necessary constants adequate experimental data is needed for each type of composite. For an infinitely dilute composite of spherical particles, the exact expression for the effective thermal conductivity is given as

$$\frac{k}{k_c} = 1 + \frac{3(k_d - k_c)}{(k_d + 2k_c)} \tag{2.4}$$

$$k_c = k_m \left[\frac{k_f + 2k_m - 2ø(k_m - k_f)}{k_f + 2k_m + ø(k_m - k_f)} \right] \tag{2.5}$$

Where K, K_c and K_d are thermal conductivities of composite, continuous-phase (matrix), and dispersed-phase (filler), respectively, and Ø is the volume fraction of the dispersed phase. Equation (2.4) and (2.5) is the well-known Maxwell equation [91] for dilute composites. Russell developed one of the early model systems using the electrical analogy. Assuming that the discrete phase and is isolated cubes of the same size dispersed in the matrix material and the isothermal lines are plane, he derived an equation (2.6) for the thermal conductivity of the composite, using a series parallel network (Tavman I.H, 1998).

$$k_c = k_m \left[\frac{\phi^{\frac{2}{3}} + \frac{k_m}{k_f}\left(1 - \phi^{\frac{2}{3}}\right)}{\phi^{\frac{2}{3}} - \phi + \frac{k_m}{k_f}\left(1 + \phi - \phi^{\frac{2}{3}}\right)} \right] \tag{2.6}$$

Lewis and Nielsen [92] derived a semi-theoretical model by a modification of the Halpin–Tsai equation [93, 94] to include the effect of the shape of the particles and the orientation or type of packing for a two-phase system

$$k_c = k_m \left[\frac{1 + AB\phi}{1 - B\phi\psi} \right]$$

$$B = \frac{(k_f - k_m) - 1}{(k_f - k_m) + A}$$

$$\psi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2} \right) \phi$$

The values of **A** and $\boldsymbol{\varphi_m}$ for many geometric shapes and orientation are given in Tables 2.1 and 2.3.

Table 2.1 Value of *A* for various systems [92]

Type of dispersed phase	Direction of heat flow	*A*
Cubes	Any	2
Spheres	Any	1.5
Aggregates of spheres	Any	$(2.5/ \O_m)$ -1
Randomly oriented rods Aspect ratio=2	Any	1.58
Randomly oriented rods Aspect ratio=4	Any	2.08
Randomly oriented rods Aspect ratio=6	Any	2.8
Randomly oriented rods Aspect ratio=10	Any	4.93
Randomly oriented rods Aspect ratio=15	Any	8.38
Uniaxially oriented fibers	Parallel to fibers	2L/D
Uniaxially oriented fibers	Perpendicular to fibers	0.5

Table 2.2 Value of $\O_m$ for various systems [92]

Shape of particle	Type of packing	$\O_m$
Spheres	Hexagonal close	0.7405
Spheres	Face centered cubic	0.7405
Spheres	Body centered cubic	0.60
Spheres	Simple cubic	0.524
Spheres	Random close	0.637
Rods and fibers	Uniaxial hexagonal close	0.907
Rods and fibers	Uniaxial simple cubic	0.785
Rods and fibers	Uniaxial random	0.82
Rods and fibers	Three dimensional random	0.52

The Knowledge Gap in Earlier Investigations

In the past, though a number of studies have been published on the thermal and dielectric characteristics of particulate composites, there is a huge knowledge gap that demands a well-planned and systematic research in this area of polymer composites. An exhaustive review of the published literature reveals that:

- Most of the investigations are aimed only at enhancing the thermal conductivity of the polymer rather than modifying both its thermal and dielectric nature to suit applications in electronics.

- Although a large number of particulates have been used as fillers in the past, most of them have taken epoxy or polyimide as the matrix material and there is no report available on epoxy based composites.
- The understanding of the relationship between the effective thermal conductivity of a composite material and the micro-structural properties (volume fractions, distribution of particles, aggregation of particles, properties of individual components, etc.) is far from satisfactory.

Although a great amount of work has already been devoted to this topic by a large number of researchers, many questions are still open. A comprehensive and systematic investigation on thermal and dielectric behavior of BN filled polymer composites has not adequately been performed yet. As a result, the effect of particulate fillers such as BN on thermal and dielectric characteristics of composites has remained a less researched area.

Objective of the Present Investigation

The objectives of this work are outlined as follows:

- Fabrication of a new class of composites using boron nitride as the reinforcing filler with an objective to improve the thermal properties of neat epoxy.
- Estimation of equivalent thermal conductivity of particulate-polymer composite system using Finite Element Method (FEM).
- Validation of the FEM analysis by measuring the thermal conductivity values experimentally.
- Characterization of these BN-epoxy composites and studying the effect of BN content on their thermal and dielectric properties.

Chapter Summary

This chapter has provided an exhaustive review of research works on particulate reinforced polymer composites, thermal conductivity of polymer matrix composites, on thermal conductivity models and on thermal/ dielectric nature of BN filled composites reported by various investigators. It has also clearly outlined the objectives of the present work. The next chapter discusses experimental planning, characterization details and the finite element analysis.

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Chapter 3

MATERIALS AND METHODS

Chapter 3

MATERIALS AND METHODS

This chapter describes the materials and methods used for the processing of the composites under this exploration. Its present the details of the behavior and thermal conductivity tests which the composite samples are subjected to the numerical methodology related to the determination of thermal conductivity based on finite element method is also presented in this chapter of the thesis.

3.1 Numerical Analysis: Concept of Finite Element Method (FEM) and ANSYS:

The Finite Element Method (FEM), originally introduced by Turner et al. [58] in 1956, is a powerful computational technique for approximate solutions to a variety of "real-world" engineering problems having complex domains subjected to general boundary conditions. FEM has become an essential step in the design or modeling of a physical phenomenon in various engineering disciplines. A physical phenomenon usually occurs in a continuum of matter (solid, liquid, or gas) involving several field variables. The field variables vary from point to point, thus possessing an infinite number of solutions in the domain.

The basis of FEM relies on the decomposition of the domain into a finite number of sub-domains (elements) for which the systematic approximate solution is constructed by applying the vibrational or weighted residual methods. In effect, FEM reduces the problem to that of a finite number of unknowns by dividing the domain into elements and by expressing the unknown field variable in terms of the assumed approximating functions within each element. These functions (also called interpolation functions) are defined in terms of the values of the field variables at specific points, referred to as nodes. Nodes are usually located along the element boundaries and they connect adjacent elements. The ability to discretize the irregular domains with finite elements makes the method a valuable and practical analysis tool for the solution of boundary, initial and Eigen value problems arising in various engineering disciplines.

The FEM is thus a numerical procedure that can be used to obtain solutions to a large class of engineering problems involving stress analysis, heat transfer, fluid flow etc. ANSYS is general-purpose finite-element modeling package for numerically solving a wide variety of mechanical problems that include static/dynamic, structural analysis (both linear and nonlinear), heat transfer, and fluid problems, as well as acoustic and electromagnetic problems.

3.2 Basic Steps in FEM:

The finite element method involves the following steps.

First, the governing differential equation of the problem is converted into an integral form. There are two techniques to achieve this:

(i) Weighted Residual Technique

(ii)Vibrational Technique

In vibrational technique, the calculus of variation is used to obtain the integral form corresponding to the given differential equation. This integral needs to be minimized to obtain the solution of the problem. For structural mechanics problems, the integral form turns out to be the expression for the total potential energy of the structure. In weighted residual technique, the integral form is constructed as a weighted integral of the governing differential equation where the weight functions are known and arbitrary except that they satisfy certain boundary conditions. To reduce the continuity requirement of the solution, this integral form is often modified using the divergence theorem. This integral form is set to zero to obtain the solution of the problem. For structural mechanics problems, if the weight function is considered as the virtual displacement, then the integral form becomes the expression of the virtual work of the structure.

In the second step, the domain of the problem is divided into a number of parts, called as elements. For one-dimensional (1-D) problems, the elements are nothing but line segments having only length and no shape. For problems of higher dimensions, the elements have both the shape and size. For two-dimensional (2D) or axi-symmetric problems, the elements used are triangles, rectangles and quadrilateral having straight or curved boundaries. Curved sided elements are good choice when the domain boundary is curved. For three-dimensional (3-D) problems, the shapes used are tetrahedron and parallelepiped having straight or curved surfaces. Division of the domain into elements is called a mesh. In this step, over a typical element, a suitable approximation is chosen for the primary variable of the problem using interpolation functions (also called as shape functions) and the unknown values of the primary variable at some pre-selected points of the element, called as the nodes.

Usually polynomials are chosen as the shape functions. For 1-D elements, there are at least 2 nodes placed at the endpoints. Additional nodes are placed in the interior of the element. For 2-D and 3-D elements, the nodes are placed at the vertices (minimum 3 nodes for triangles, minimum 4 nodes for rectangles, quadrilaterals and tetrahedral and minimum 8 nodes for parallelepiped shaped elements). Additional nodes are placed either on the boundaries or in the interior. The values of the primary variable at the nodes are called as the degrees of freedom.

To get the exact solution, the expression for the primary variable must contain a complete set of polynomials (i.e., infinite terms) or if it contains only the finite number of terms, then the number of elements must be infinite. In either case, it results into an infinite set of algebraic equations. To make the problem tractable, only a finite number of elements and an expression with only finite number of terms are used. Then, we get only an approximate solution. (Therefore, the expression for the primary variable chosen to obtain an approximate solution is called an approximation). The accuracy of the approximate solution, however, can be improved either by increasing the number of terms in the approximation or the number of elements.

In the fourth step, the approximation for the primary variable is substituted into the integral form. If the integral form is of vibrational type, it is minimized to get the algebraic equations for the unknown nodal values of the primary variable. If the integral form is of the weighted residual type, it is set to zero to obtain the algebraic equations. In each case, the algebraic equations are obtained element wise first (called as the element equations) and then they are assembled over all the elements to obtain the algebraic equations for the whole domain (called as the global equations). In this step, the algebraic equations are modified to take care of the boundary conditions on the primary variable. The modified algebraic equations are solved to find the nodal values of the primary variable.

In the last step, the post-processing of the solution is done. That is, first the secondary variables of the problem are calculated from the solution. Then, the nodal values of the primary and secondary variables are used to construct their graphical variation over the domain either in the form of graphs (for 1-D problems) or 2-D/3-D contours as the case may be.

3.3 Advantages of the finite element method over other numerical methods are as follows:

- In FEM no geometric restriction, it can be applied the body or region with any shape of product.
- Boundary loading and conditions are not restricted (boundary condition and load may be applied to any portion of the body.
- Domains problem consisting of more than one material (composite) can be easily analyzed.
- The method can be used for any irregular-shaped domain and all types of boundary conditions.
- Accuracy of the solution can be improved either by proper refinement of the mesh or by choosing approximation of higher degree polynomials.

The algebraic equations can be easily generated and solved on a computer. In fact, a general purpose code can be developed for the analysis of a large class of problems.

- FEM structures are closely resembled the actual body or region to be analyzed.
- The analysis result is easily improved by mesh refinement.
- In the finite element method it is easy to produce detailed visualizations of a complex problem.

3.4 MATERIALS:

(a)Matrix Material: Epoxy resins are the most commonly used resins. Epoxy LY 556 resin, chemically belonging to the “epoxide” family is used as the matrix material. The low temperature curing epoxy resin (Araldite LY 556) and the corresponding hardener (HY 951) are mixed in a ratio of 10:1 by weight as recommended.They are low molecular weight organic liquids containing epoxide groups. Epoxy is chosen primarily because it happens to the most commonly used polymer and because of its low density (1.1 gm. /cc). Epoxide has three members in its ring: one oxygen and two carbon atoms. The reaction of epichlorohydrin with phenols or aromatic amines makes most epoxies.Low value of thermal conductivity of epoxy is about (0.363W/m. K).

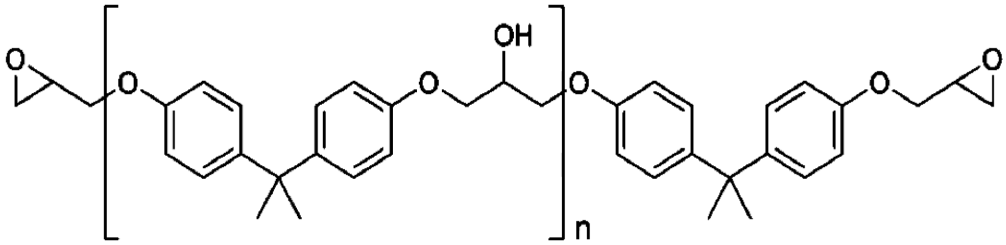

Fig 3.1: Unmodified epoxy pre polymer resin chain.
(‘n’ denotes number of polymerized unit)

Fig 3.2: Epoxy Resin

(b)Filler material :-(BN) Boron nitride is a white solid material in the as produced hot pressed pattern. It is a low porosity solid and easily machined into complex shapes using standard carbide tooling. The composites are anisotropic in its electrical and mechanical properties due to the platy hexagonal crystals and their orientation during the hot press consolidation. Its thermal conductivity and density values are (110W/m .K and 2.34gm/cc respectively).

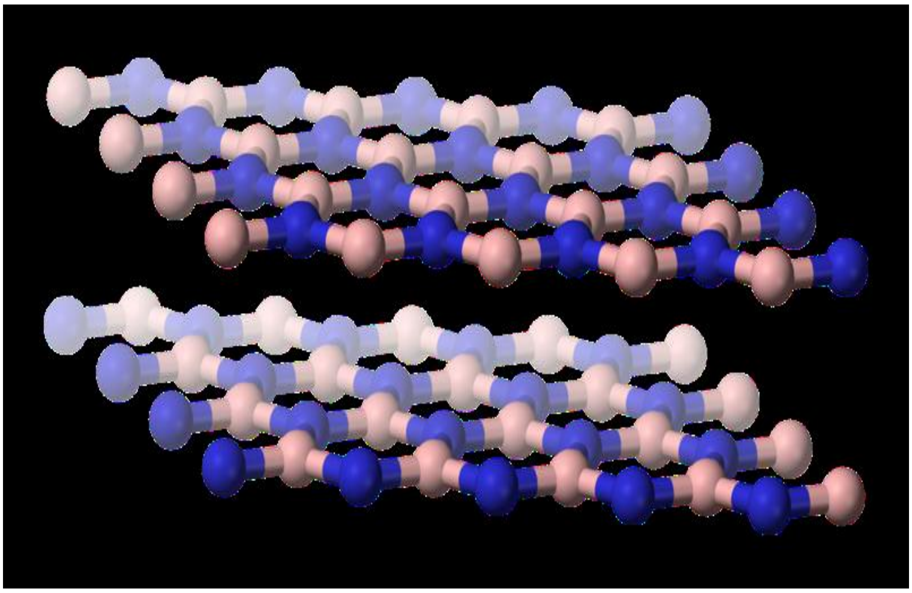

Fig 3.3: Hexagonal crystalline form of Boron Nitride (h-BN or α-BN)

Key Properties:

- High thermal conductivity,
- Low thermal expansion,
- Good thermal shock resistance
- High electrical resistance
- Low density.
- Non-toxic

Boron nitride is often referred to as "white graphite" because it is a lubricious material with the same platy hexagonal structure as carbon graphite. BN is a very good electrical insulator, offer very high thermal conductivity and good thermal shocking resistance. BN is stable inert in nature and reducing atmospheres up to 2800°C, and in oxidizing atmospheres to 850°C.Three grades are commonly used, including calcium borate binder system, boric oxide binder system, and a pure diffusion bonder grade. The boric oxide contains material (Grade BO) absorbs moisture which causes swelling and property reduction. The calcium borate contains material (Grade CA) is moisture resistant. The pure BN material (Grade XP) contains no binders and is used for extremes of temperature and where purity is important. The boric oxide materials are the most commonly used grade.

3.5 METHOD:

Composite fabrication:

- The composites are cast by conventionally hand-lay-up techniques so as to get six composite samples with different filler concentrations.
- The low temperature epoxy resins and corresponding hardener (HY951) are mixed in a ratio of 10:1 micro-sized boron nitride particles with average size of 100 µm .
- Composites of six different compositions 0, 1.4,3.35,5.23,7.85,9.04 and 11.3 vol% of boron nitride are made.
- The casting are left cure at room temperature for about 24 hours after which the cups are broken and samples are released

Samples	Composition (for BN filled epoxy)
1	Epoxy + 0 vol. % (0 wt %) BN Filler
2	Epoxy + 1.4 vol. % (2.93wt %) BN Filler
3	Epoxy + 3.35vol. % (6.867wt %) BN Filler
4	Epoxy + 5.26vol. % (10.50wt %) BN Filler
5	Epoxy + 7.85vol. % (15.34wt %) BN Filler
6	Epoxy + 9.04vol. % (18.08wt %) BN Filler
7	Epoxy + 11.3vol. % (21.32wt %) BN Filler

Table 3.1: List of particulate filled composites fabricated by hand-lay-up techniques.

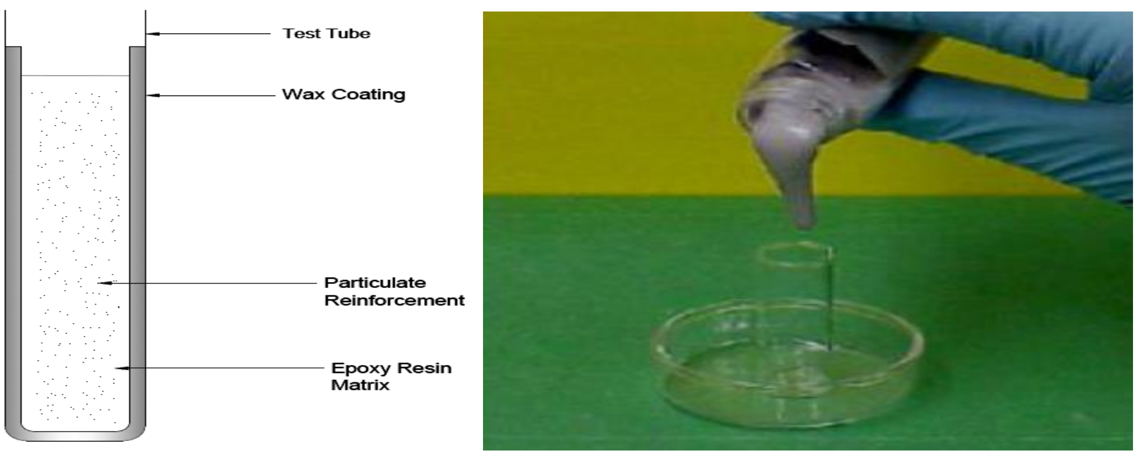

Fig. 3.4 Preparation of particulate filled composites by hand-lay-up technique

3.6 Experimental Determination of Thermal Conductivity:

Unitherm™ Model 2022 is used to measure thermal conductivity of a variety of materials. These include polymer, ceramics, composites, glasses, rubbers, some metals and other materials of low to medium thermal conductivity. Only relatively small test samples are required. Non- solids such as pastes or liquids can be tested using particular containers. Thin films can also be tested accurately using multi-layer techniques. The tests are in accordance with **ASTM E-1530** standard.

Operating principle of Unitherm™2022:

A sample of the material is held under a uniform compressive load between two polished surfaces, each part controlled at different temperatures. The lower surface is part of a calibrated heat flow transducer. The heat flow from upper surface passes through the sample, to the lower surface establishing an axial temperature gradient in the stack. After attain thermal equilibrium, the temperature differences across the sample is measured along with the output from the heat flow transducer. These values and the samples thickness are then used to calculate the thermal conductivity. The temperature drops through the sample is measured with temperature sensors in the highly conductive metal surface layers on either side of the sample. The heat conduction is measured by:

$$\boldsymbol{Q} = KA\frac{\boldsymbol{T_1 - T_2}}{\boldsymbol{x}} \tag{3.1}$$

Where Q is the heat flux (W), K is the thermal conductivity (W/m-K), A is the cross-sectional area (m^2), T_1-$T_2$is the difference in temperature (K), x is the thickness of the sample (m). The thermal resistance of a sample can be given as,

$$\boldsymbol{R} = \frac{\boldsymbol{x}}{\boldsymbol{KA}} \tag{3.2}$$

Where, R is the resistance of the sample between hot and cold surfaces (m^2-K/W).From Equation 3.2 we can write that

$$\boldsymbol{K} = \frac{x}{RA} \tag{3.3}$$

Fig3.5**:** Determination of thermal conductivity using unitherm™ model 2022

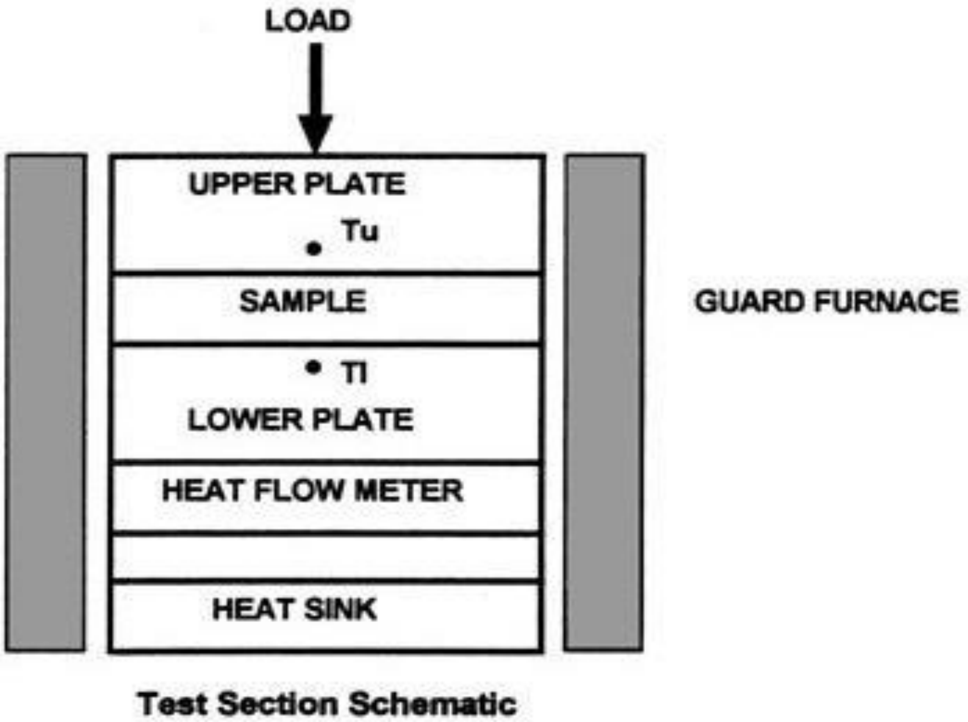

Fig.3.6. Schematic model showing the system arrangement in Unitherm 2022

In Unitherm 2022, the heat flux transducer measures the Q value and the temperature difference can be obtained between the lower plate and upper plate. Thus the thermal resistance can be calculated between the upper surface and lower surfaces. Adding the input value of thickness and taking the known cross- sectional area and the thermal conductivity of the samples can be calculated using Equation 3.3.

Chapter Summary

This chapter has provided:

- An explanation of the finite element method
- The descriptions of materials used in the experiments
- The details of fabrication of the composites by hand-lay-up technique
- The description of thermal conductivity and dielectric property measurement

The next chapter presents the results of the numerical analysis and experiments conducted to measure the thermal conductivity and dielectric characteristics of the polymer composites under study.

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Chapter 4

RESULTS AND DISCUSSION

Chapter 4

RESULTS AND DISCUSSION

This chapter presents the results of the numerical analysis and experiments conducted to study the thermal conductivity of the polymer composites under study. It also presents the test results for other thermal properties and dielectric characterization of these composites.

PART 1

4.1 EFFECTIVE THERMAL CONDUCTIVITY (K_{EFF}) OF BORON NITRIDE FILLED WITH EPOXY MATRIX COMPOSITES:

4.1.1 Description of the problem:

The determination of effective properties of composite materials is of paramount importance for functional design and application of composite materials. One of the important factors that influence the effective properties and can be controlled to an appreciable extent is the microstructure of the composite. Here, microstructure means the shape, size distribution, spatial distribution and orientation distribution of the reinforcing inclusion in the matrix. Although most composite possess inclusion of random distributions, great insight of the effect of microstructure on the effective properties can be gained from the investigation of composites with periodic structure. System with periodic structures can be more easily analyzed because of the high degree of symmetry embedded in the system.

Using the finite-element program ANSYS, thermal analysis is carried out for the conductive heat transfer through the composite body. In order to make a thermal analysis, three-dimensional physical models with spheres-in-a-cube lattice array have been used to simulate the microstructure of composite materials for six different filler concentrations. Furthermore, the effective thermal conductivities of these epoxy composites filled with boron nitride up to about 11.3% by volume is numerically determined using ANSYS.

4.1.2 Assumptions:

In the analysis of the ideal case it will be assumed that

1. The composites are macroscopically homogeneous.
2. Locally both the matrix and filler are homogeneous and isotropic.
3. The thermal contact resistance between the filler and the matrix is negligible.
4. The composite lamina is free of voids.
5. The problem is based on 3D physical model.
6. The filler particles are in a square periodic array or uniform dispersed in matrix.

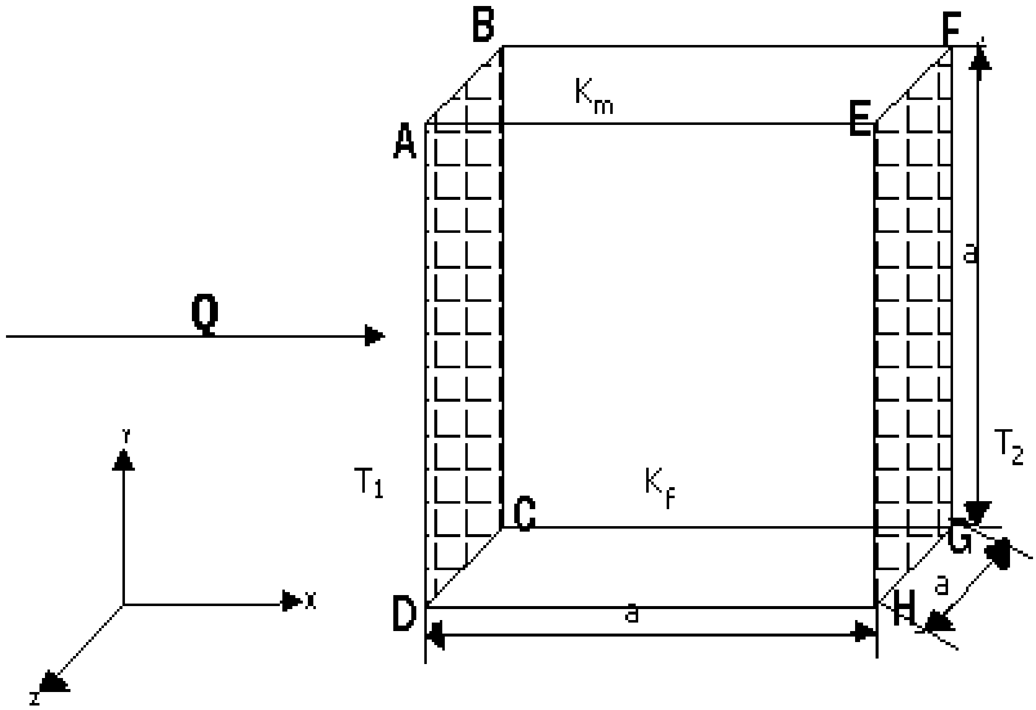

Fig.4.1 Boundary conditions

4.1.3 Numerical Analysis

In the numerical analysis of the heat conduction problems, the temperatures at the nodes along the surfaces ABCD is prescribed as T1 (=100° C) and the convective heat transfer coefficient is assumed to be 2.5 W/m^2-K at ambient temperature of 27°C. The heat flow direction and the boundary conditions are shown in Fig. 4.1.

The others surfaces parallel to the direction of the heat flow are all assumed adiabatic. The temperatures at the nodes in the interior region and on the adiabatic boundaries are unknown. These temperatures are obtained with the help of finite-element program package ANSYS.

Thermal conductivities of epoxy composites filled with boron nitride particles up to 11.3 % by volume are numerically estimated by using the spheres-in-cube model. A typical 3-D model showing arrangement of spherical fillers with a particle concentration of 1.4 vol% within the cube shaped matrix body is illustrated in Fig.4.2. The temperature profiles obtained from FEM analysis for the composites (spheres-in cube arrangement) with particulate concentrations of 1.4, 3.35, 5.23, 7.85, 9.04 and 11.3 vol. % are presented in Fig. 4.3 - Fig.4.8 respectively.

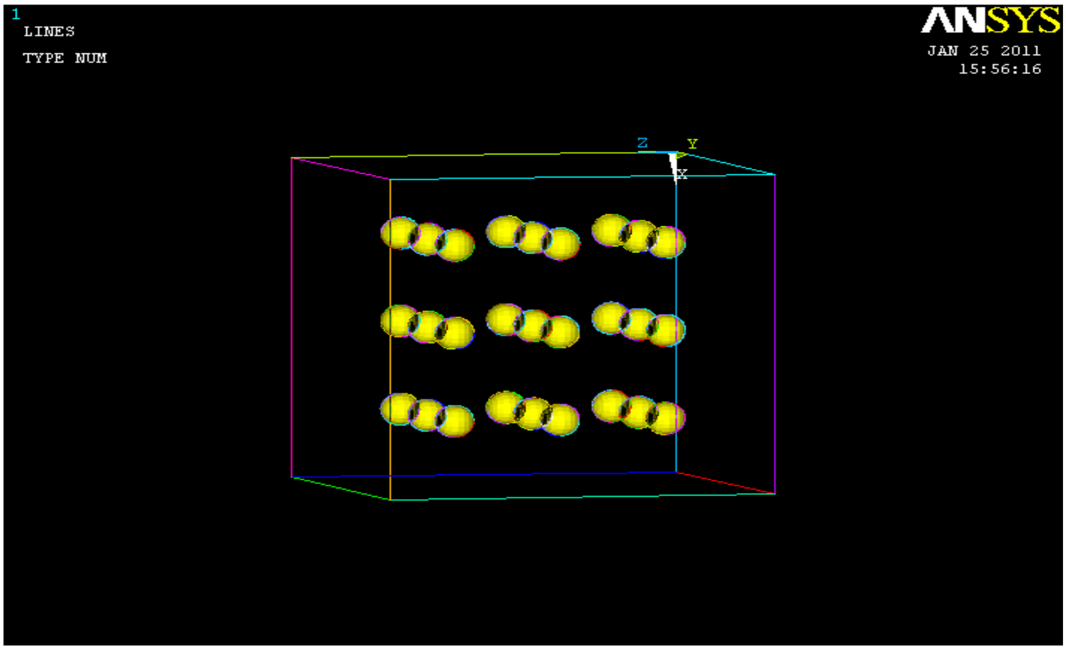

Fig 4.2: Geometric model of boron nitride (spheres) in epoxy matrix (cube) at 3.35vol%.

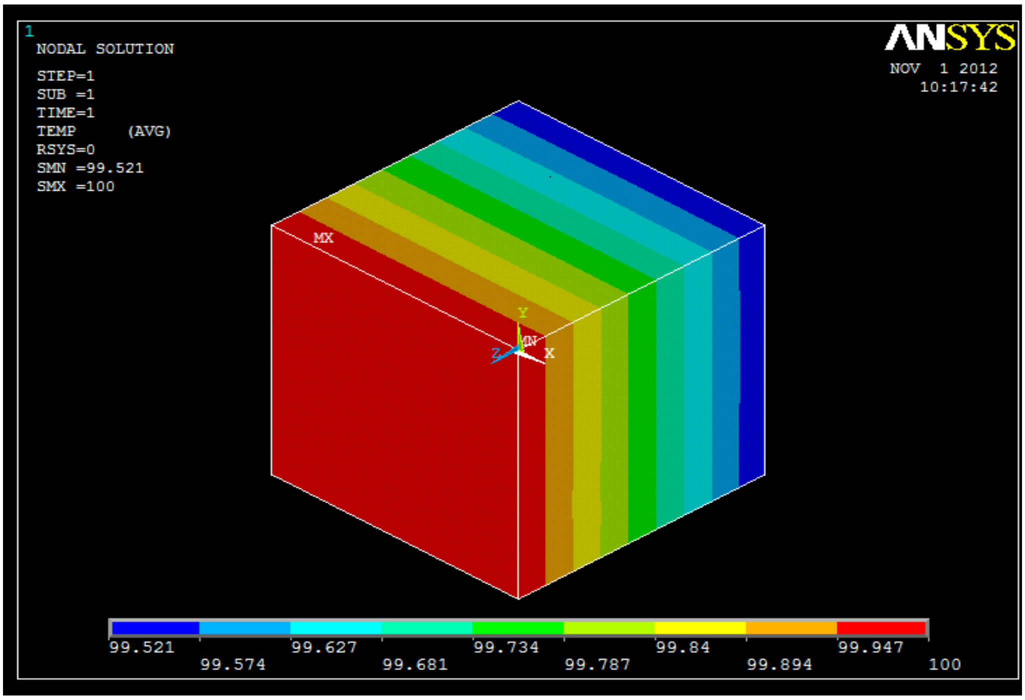

Fig 4.3: Temperature profile for composite with particle concentration of 1.4vol%.

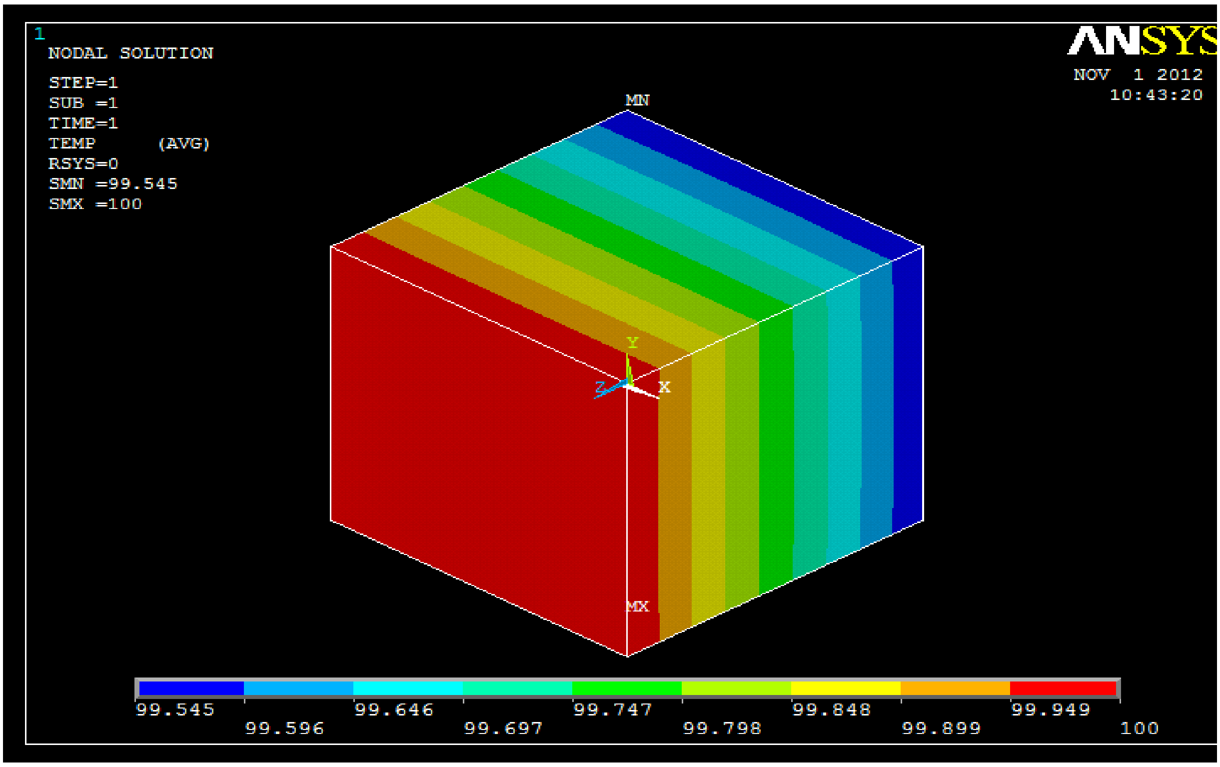

Fig 4.4: Temperature profile for composite with particle concentration of 3.35vol%.

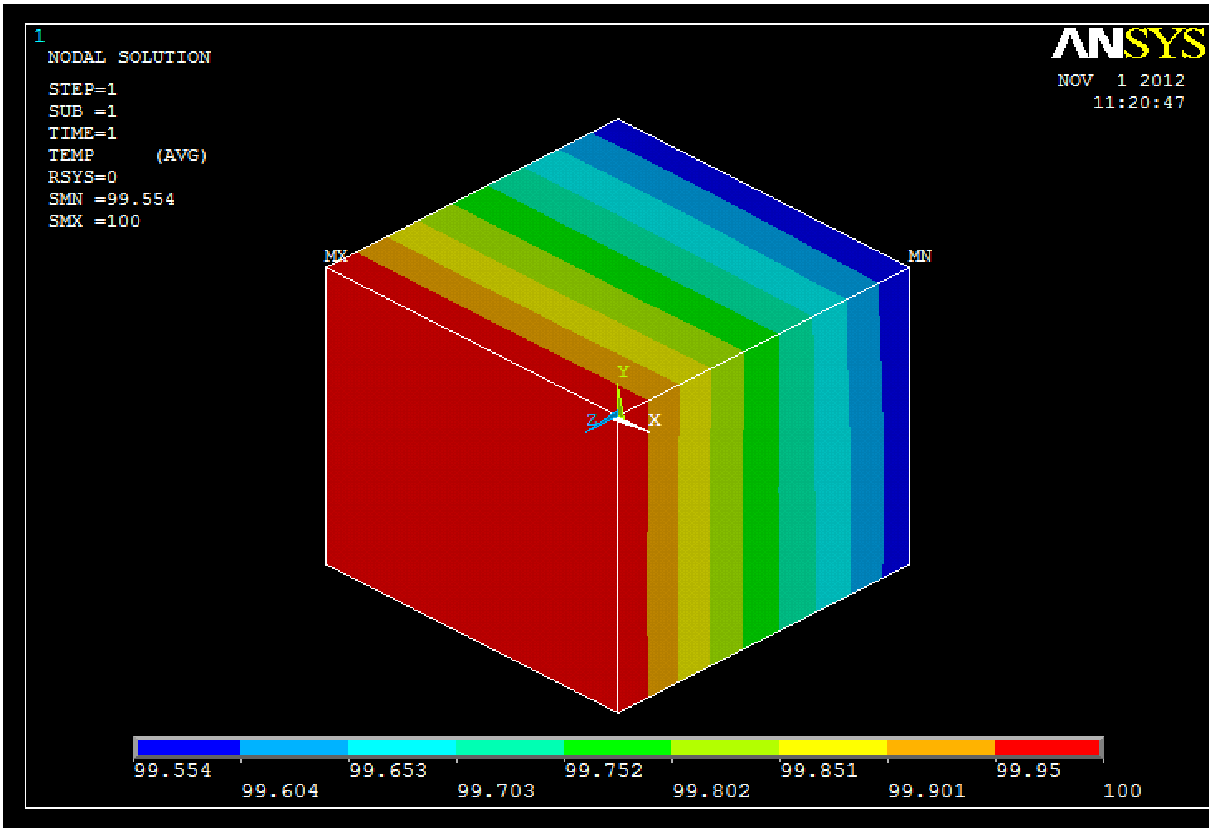

Fig 4.5: Temperature profile for composite with particle concentration of 5.23vol%.

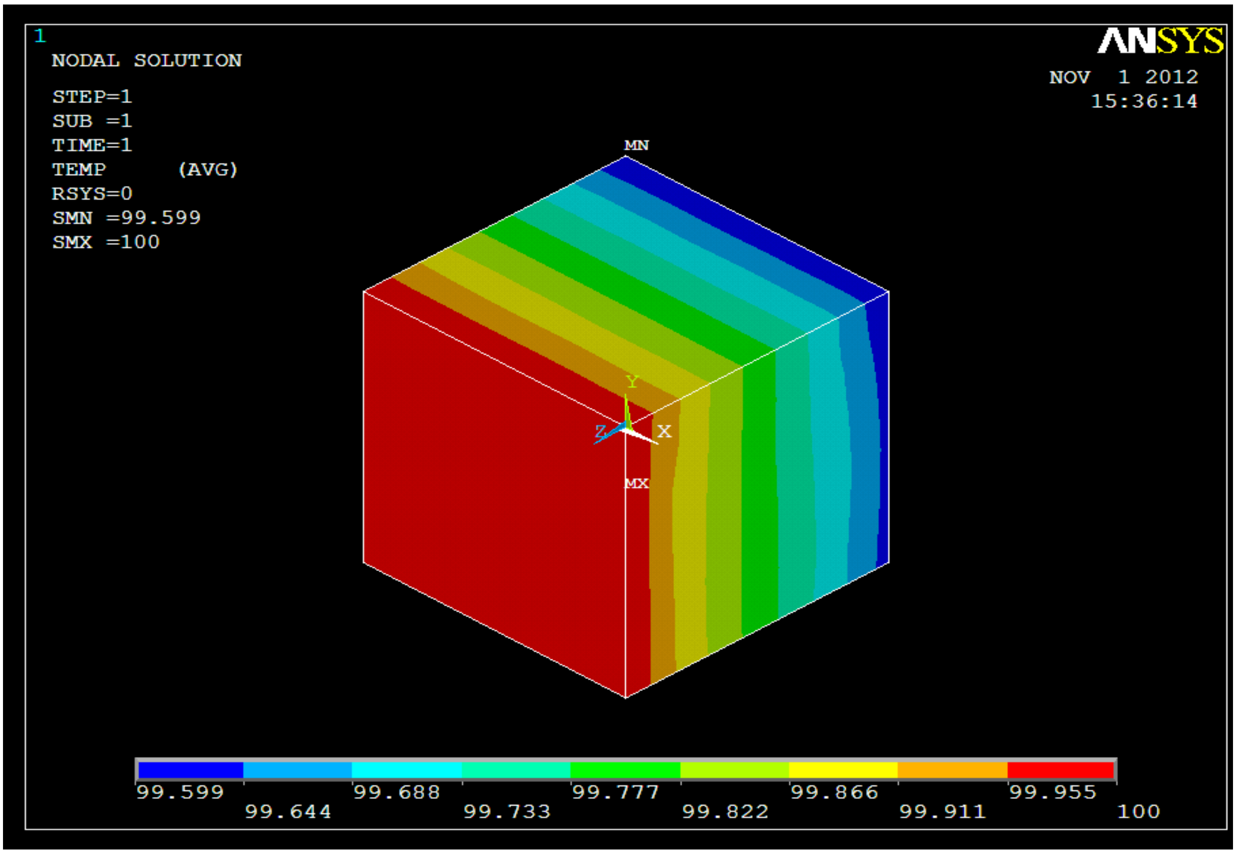

Fig 4.6: Temperature profile for composite with particle concentration of 7.85vol%.

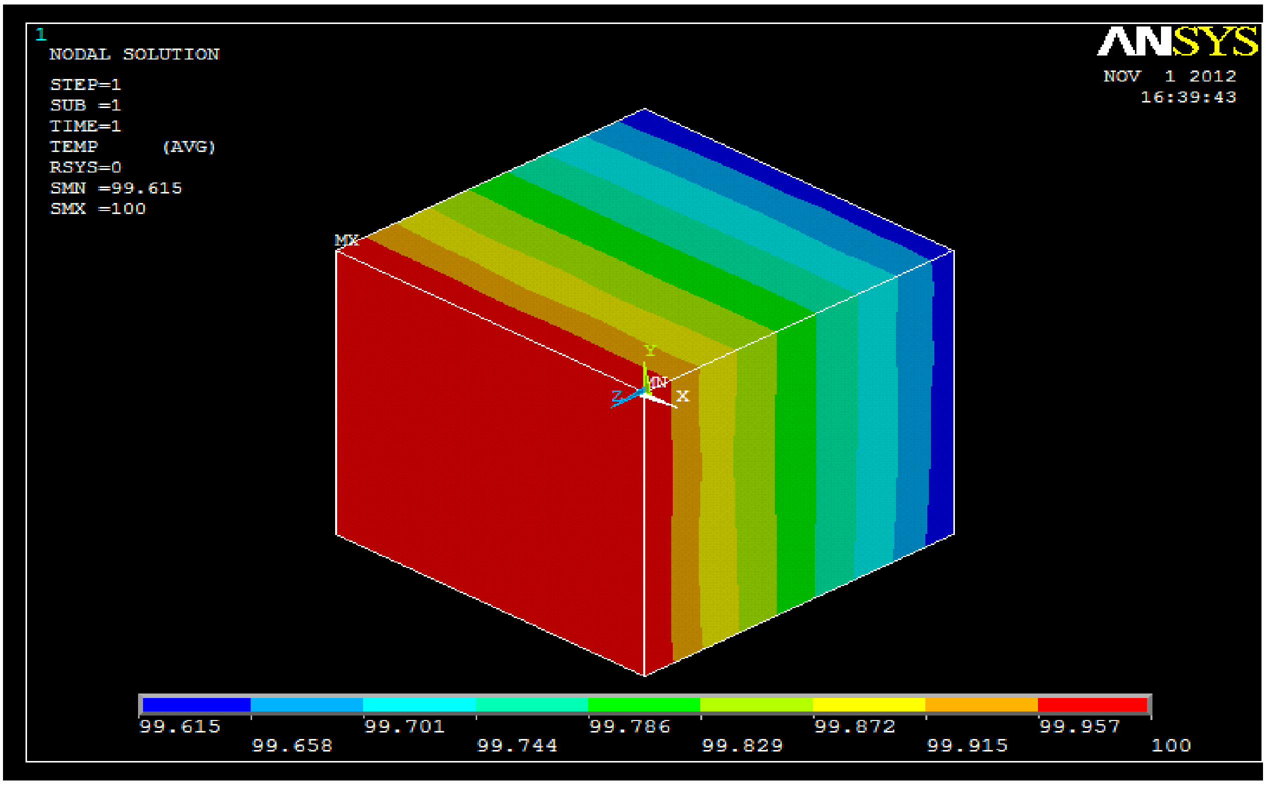

Fig 4.7: Temperature profile for composite with particle concentration of 9.04vol%.

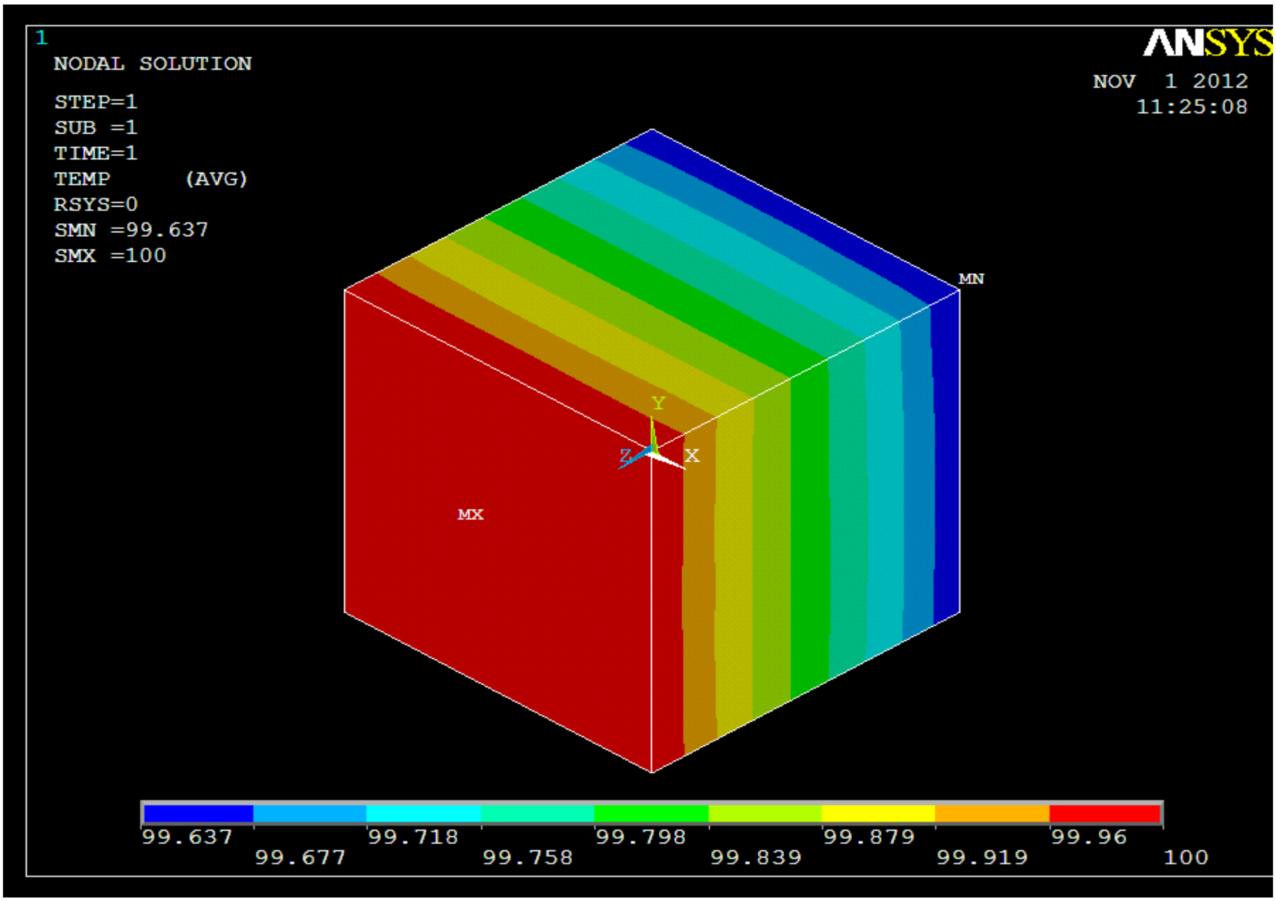

Fig 4.8: Temperature profile for composite with particle concentration of 11.3vol%.

The values of effective thermal conductivities of the particulate filled epoxy composites with varied proportions of boron nitride obtained using rule-of-mixture model, Maxwell's equation, Lewis and Nielsen's equation and ROM series model and Geometric model are presented in Table 4.1. It presents a comparison among the results obtained using these models with regard to the corresponding values of effective conductivity obtained experimentally.

Table 4.1: Effective thermal conductivity values obtained from different methods.

Sample No.	Boron nitride (Vol. %)	Effective thermal conductivity of the composite [W/m.K]				
		ROM series model	Maxwell model	Lewis-Nielsen Model	Geometric Model	Experimental
1	1.4	0.368	0.378	0.385	0.393	0.372
2	3.35	0.376	0.400	0.419	0.439	0.401
3	5.23	0.383	0.422	0.456	0.489	0.407
4	7.85	0.394	0.454	0.514	0.568	0.432
5	9.04	0.398	0.469	0.545	0.608	0.442
6	11.3	0.410	0.499	0.611	0.692	0.464

Table 4.2: Percentage error of different models with respect to experimental values.

Sample No.	Boron nitride (Vol. %)	Percentage errors with respect to the experimental value (%)				
		ROM series model	Maxwell model	Lewis-Nielsen Model	Geometric Model	Experimental
1	1.4	1.075	-1.613	-3.495	-5.645	0.372
2	3.35	6.234	.2494	-4.489	-9.476	0.401
3	5.23	5.896	-3.685	-12.039	-20.147	0.407
4	7.85	8.796	-5.093	-18.981	-31.48	0.432
5	9.04	9.954	-6.109	-23.30	-37.55	0.442
6	11.3	11.637	-7.543	-31.68	-49.13	0.464

Table 4.3Thermal conductivity values for composites obtained from FEM and Experiment

Sample No.	Boron nitride (Vol. %)	Effective thermal conductivity of composites K_{eff} (W/m-K)		Percentage errors with respect to the experimental value (%)
		FEM (Spheres-in-cube Model)	Experimental	
1	1.4	0.368	0.372	1.075
2	3.35	0.369	0.401	7.980
3	5.23	0.4025	0.407	1.106
4	7.85	0.424	0.432	1.852
5	9.04	0.4335	0.442	1.923
6	11.3	0.4545	0.464	2.047

The simulated values of effective thermal conductivity of the composites obtained by FEM analysis are presented in Table 4.3 along with the corresponding measured values. The findings for spheres-in-cube arrangements are found to be different as seen in this table.

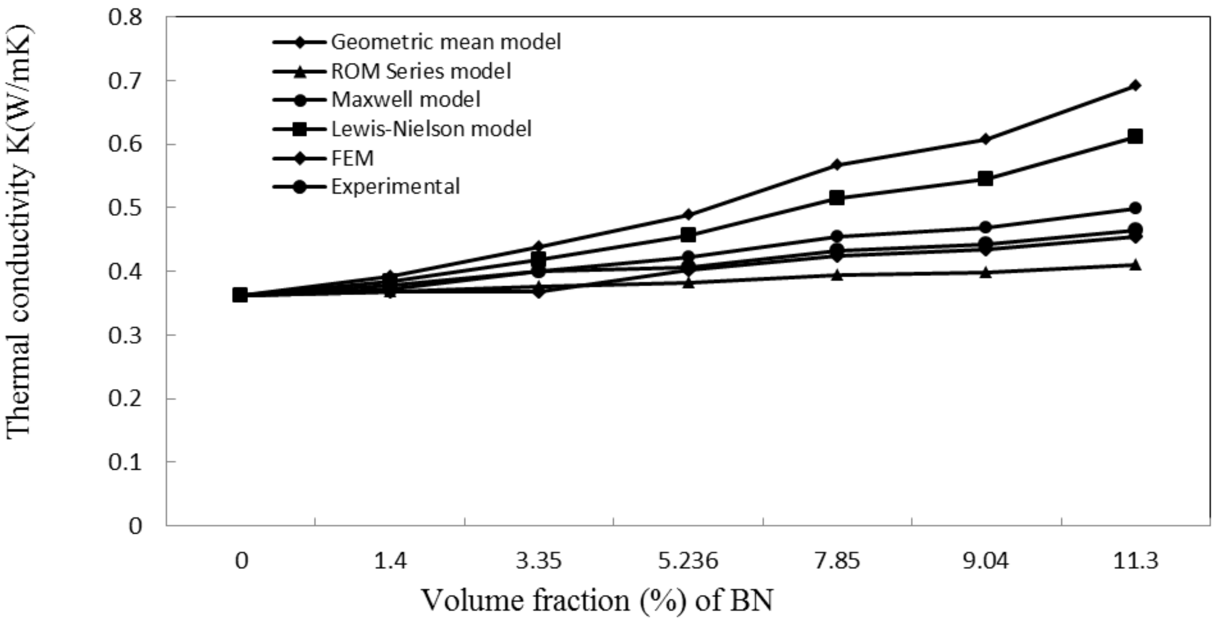

Fig. 4.9: Comparison of thermal conductivity values obtained from different methods.

It is noticed that while the FEM analysis can very well be used for predictive purpose in determining the effective thermal conductivity for a wide range of particle concentrations.

The difference between the FEM simulated values and the values obtained by Rule of mixture and Maxwell's model may be attributed to the fact that these models do not consider the distribution pattern of the filler particles within the matrix body, which the FEM analysis does. With addition of 11.3% of 100 micron size boron nitride particle, thermal conductivity of epoxy increased from 0.363W/m-K to 0.464W/m-K. It can be seen from the graph that for less filler concentration, the slope of the curve is less and as the filler volume fraction increases, the curves representing FEM become steeper. It might be due to the fact that with increase in filler concentration, the inter-particle distance reduces and the conductive chains begin to form which increase the thermal conductivity quite reason.

Fig. 4.10 presents a comparative picture of the thermal conductivity values obtained from different methods. It is noticed that the results obtained from the finite-element analysis taking sphere-in-cube composite model are closer to the measured values of effective thermal conductivity for composites of different filler content. The percentage errors associated with the FEM values with respect to the experimental values are given in Table 4.3. It is seen from this table that while the errors associated with sphere-in-cube model simulations lie in the range 1-3 %.

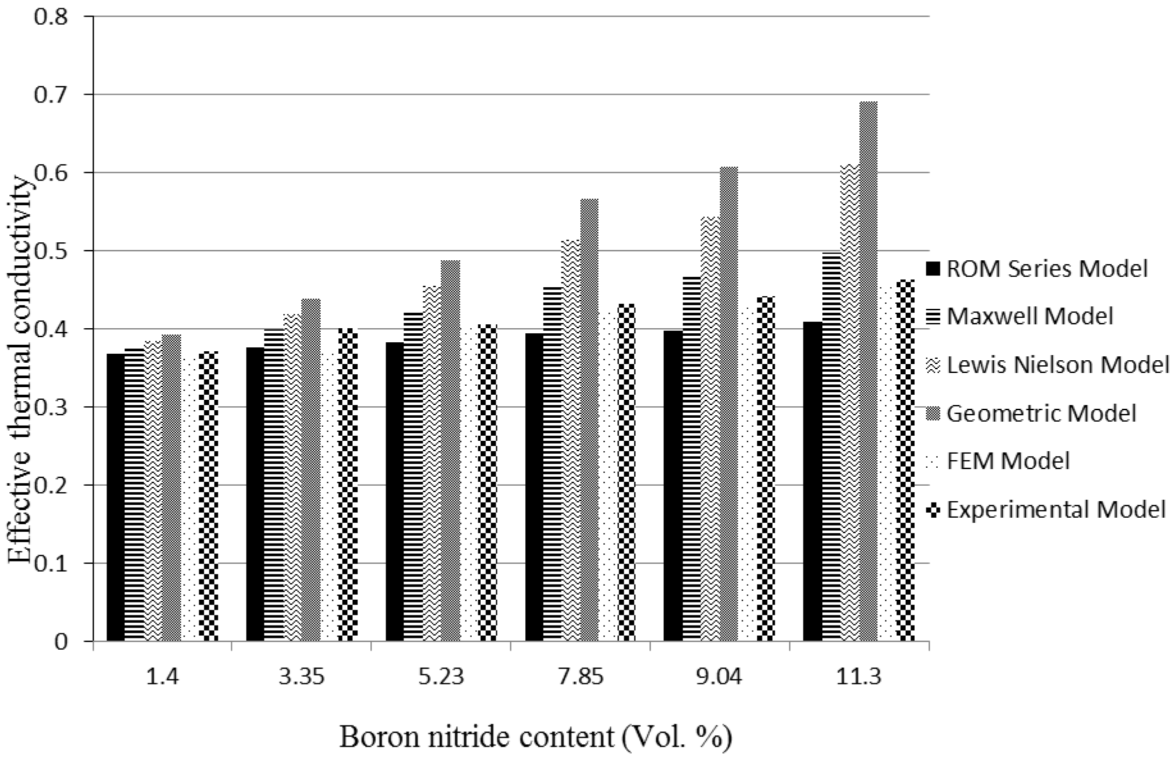

Fig. 4.10: Comparison of thermal conductivity values obtained from different methods.

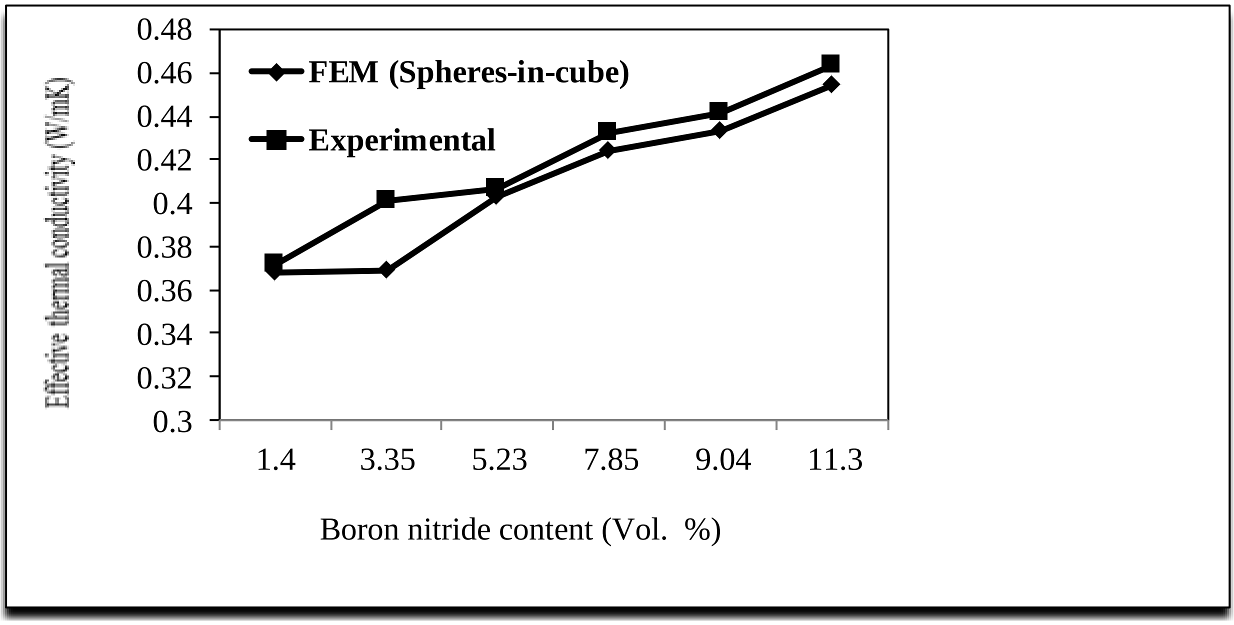

Fig. 4.11: Effective thermal conductivity of the composites as function of BN content

On comparing with the experimentally measured values, it is further noticed that while the rule-of-mixture, Maxwell's equation, Lewis and Nielsen's equation (spheres-in-cube model), Lewis and FEM (spheres-in-cube model) underestimate the value of thermal conductivity, FEM (sphere-in-cube) overestimates the value with respect to the experimental ones. It leads to a conclusion that for a particulate filled composite of this kind the FEM (sphere-in-cube model) can very well be used for predictive purpose in determining the effective thermal conductivity for a wide range of particle concentration. Fig. 4.13 compares the FEM (sphere-in-cube model) simulated results of thermal conductivity with those found from experiments. It also presents the variation of effective thermal conductivity as a function of the boron nitride content in the composite.

The difference between the measured values and the simulated value of conductivity may be attributed to the fact that some of the assumptions taken for the numerical analysis are not real. The shape of BN is assumed to be spherical, while in actual practice they are of irregular shaped. Moreover, although the distribution of boron nitride particulates in the matrix body is assumed to be in an arranged manner, it is actually dispersed in the resin randomly. It is encouraging to note that the incorporation of boron nitride results in enhancement of thermal conductivity of epoxy resin. With addition of 1.4 vol. % of BN, the thermal conductivity increased by about 2.47 % and with addition of 11.3% of BN, the thermal conductivity increased by about 27.82 % when compared with neat epoxy resin.

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Chapter 5

CONCLUSIONS AND SCOPE FOR FUTURE WORK

Chapter 5

CONCLUSIONS AND SCOPE FOR FUTURE WORK

The research presented in this thesis consists of two parts:

1. The first part describes the detailed fabrication of a series of epoxy based composites filled with micro-sized boron nitride particles in different weight proportions by hand lay-up technique.
2. The second part includes an assessment of the effective thermal conductivity of these composites using finite element method. The results are validated by simultaneous measurement of thermal conductivity of the composites in the laboratory using a Unitherm™ Model 2022 test set up.

As already mentioned earlier, electronic devices are packaged with many polymeric materials, such as electronic molding compound and glob top encapsulation. Another common application area is the printed circuit boards. A printed circuit board (PCB), is used to mechanically support and electrically connect electronic components using conductive pathways, tracks or signal traces. Printed circuit boards are used virtually in all commercially-produced electronic devices. Although polymeric resin systems are used for PCB substrates and for encapsulating a variety of electronic components because of their high thermal stability, moisture resistance, low dielectric constant and low cost, unfortunately, they have poor thermal properties like low thermal conductivity. So, thermally conducting, but electrically insulating, polymer matrix composites are becoming increasingly important for this kind of applications because the heat dissipation ability limits the reliability, performance and miniaturization of electronics. In view of this, the present research has been focused on evaluating the two key characteristic features: thermal conductivity and dielectric constant of BN filled polymers. Some of the important findings of this research are listed below.

5.1 Conclusions:

This investigation has led to the following specific conclusions:

1. Successful fabrication of micro sized BN filled epoxy composites by hand-lay-up technique is possible.

2. Finite element method (FEM) can be gainfully employed for determination of effective thermal conductivity of these composites with different amount of BN content.

3. The values of effective thermal conductivity obtained for various composite models from FEM are in reasonable agreement with the experimental values for a wide range of filler contents from 1.4 vol. % to 11.3 vol. %.

4. The values of thermal conductivity obtained from FEM (sphere-in-cube arrangement) are found to be more accurate (with respect to the experimental values) than the calculated values from existing theoretical models such as Rule of mixture, Maxwell's equation, Lewis and Nielsen's model, Bruggeman's model .

5. Incorporation of micro-sized BN results in significant increase of thermal conductivity of epoxy resin. With addition of 1.4 vol. % of BN, the thermal conductivity of epoxy increases by about 2.47% and with addition of 11.3 vol. % of BN the increases by about 27.82%. Similarly,

6. With increased thermal conductivity and controlled dielectric constant, this new class of BN filled epoxy composites can be used for applications such as electronic packages, encapsulations, die (chip) attachments, thermal grease, thermal interface materials and electrical cable insulation.

7. Incorporation of BN results in enhancement of thermal conductivity of epoxy resin and there by improves its heat conduction capability.

5.2 Scope for future work:

This work leaves a wide scope for future investigators to explore many other aspects of thermal behavior of particulate filled composites. Some recommendations for future research include: Effect of filler shape and size on thermal properties of the composites Exploration of new fillers and polymers for development of materials having high thermal conductivity and low electrical conductivity.

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